

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
21 November 2002 (21.11.2002)

PCT

(10) International Publication Number
WO 02/092864 A2

- (51) International Patent Classification⁷: C22C 1/04
- (21) International Application Number: PCT/JP02/04644
- (22) International Filing Date: 14 May 2002 (14.05.2002)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
- | | | |
|-------------|------------------------------|----|
| 2001-145571 | 15 May 2001 (15.05.2001) | JP |
| 60/291,925 | 21 May 2001 (21.05.2001) | US |
| 2001-340318 | 6 November 2001 (06.11.2001) | JP |
| 60/331,200 | 9 November 2001 (09.11.2001) | US |
- (71) Applicant (*for all designated States except US*): SHOWA DENKO K. K. [JP/JP]; 13-9, Shiba Daimon 1-chome, Minato-ku, Tokyo 105-8518 (JP).
- (72) Inventors; and
- (75) Inventors/Applicants (*for US only*): OMORI, Kazuhiro [JP/JP]; Corporate R & D Center, Showa Denko K.K., 5-1, Okawa-cho, Kawasaki-ku, Kawasaki-shi, Kanagawa 210-0858 (JP). NAITO, Kazumi [JP/JP]; Central Research Laboratory, Showa Denko K. K., 1-1, Ohnodai 1-chome, Midori-ku, Chiba-shi, Chiba 267-0056 (JP). KAWASAKI, Toshiya [JP/JP]; Corporate R & D Center, Showa Denko K.K., 5-1, Okawa-cho, Kawasaki-ku, Kawasaki-shi, Kanagawa 210-0858 (JP). WADA, Kouichi [JP/JP]; Corporate R & D Center, Showa Denko K.K.,
- (54) Title: NIOBIUM POWDER, NIOBIUM SINTERED BODY AND CAPACITOR USING THE SINTERED BODY
- (57) Abstract: A niobium powder for a capacitor having a tapping density of 0.5 to 2.5 g/ml, and average particle size of 10 to 1000 μm , angle of repose from 10° to 60°, the BET specific surface area from 0.5 to 40 m^2/g and a plurality of pore diameter peak tops in the pore distribution, and a producing method thereof; (2) a niobium sintered body, which is obtained by sintering the above niobium powder and, having a plurality of pore diameter peak tops in a range of 0.01 μm to 500 μm , preferably, the peak tops of two peaks among the plurality of pore diameter peak tops having a highest relative intensity are present in the range of 0.2 to 0.7 μm and in the range of 0.7 to 3 μm , respectively, and a producing method thereof; (3) a capacitor using the above sintered body and a producing method thereof; and (4) an electronic circuit and electronic device using the above capacitor.



WO 02/092864 A2

5-1, Okawa-cho, Kawasaki-ku, Kawasaki-shi, Kanagawa 210-0858 (JP).

(74) Agent: OHIE, Kunihisa; Ohie Patent Office, Horiguchi No. 2, Building 71; 2-6, Nihonbashi-Ningyocho 2-chome, Chuo-ku 103-0013 (JP).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EB, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, KE, KG, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

DESCRIPTION

Niobium Powder, Niobium Sintered Body and Capacitor Using
the Sintered Body

5

CROSS REFERENCE TO THE RELATED APPLICATIONS

This is an application based on the prescription of 35 U.S.C. Section 111(a) with claiming the benefit of filing date of U.S. Provisional application Serial No. 60/291,925 10 filed May 21, 2001 and Serial No. 60/331,200 filed November 9, 2001 under the provision of 35 U.S.C.111(b), pursuant to 35 U.S.C. Section 119(e) (1).

TECHNICAL FIELD

15 The present invention relates to a niobium powder and a sintered body thereof, which can stably produce a capacitor having a large capacitance per unit mass, good leakage current characteristics and excellent moisture resistance, and also relates to a capacitor using the 20 niobium powder and sintered body and production methods of niobium powder, sintered body and the capacitor.

BACKGROUND ART

Capacitors for use in electronic instruments such as 25 portable telephone and personal computer are demanded to have a small size and a large capacitance. Among these capacitors, a tantalum capacitor is preferred because of

its large capacitance for the size and good performance.

Moreover, recent electronic devices are demanded to operate at a low voltage and high frequency with low noise, and also a lower equivalent series resistance (ESR) is 5 required for a solid electrolyte capacitor.

In this tantalum capacitor, a sintered body of tantalum powder is generally used for the anode moiety. This powder is molded and then sintered, whereby the powder is integrated and works out to an electrode called a 10 sintered body. The inside of this sintered body takes a three-dimensional complicated form resulting from the particles of the powder being electrically and mechanically connected with each other. On the surface of this sintered body including the surface of the inside void, a dielectric 15 film layer is formed and thereinto, a material as a counter electrode is impregnated, whereby a capacitor is fabricated. As long as the dielectric film layer uniformly adheres to the inside or outside surface of the sintered body, the capacitance of the capacitor manufactured greatly depends 20 on, microscopically, the contact state of the counter electrode material with the dielectric film layer.

In order to increase the capacitance of the tantalum capacitor, it is necessary to increase the mass of the sintered body or to use a sintered body increased in the 25 surface area by pulverizing the tantalum powder.

The method of increasing the mass of the sintered body necessarily involves enlargement of the capacitor shape and

cannot satisfy the requirement for downsizing. On the other hand, in the method of pulverizing tantalum powder to increase the specific surface area, the pore diameter of the tantalum sintered body decreases or closed pores 5 increase at the stage of sintering, as a result, impregnation of the cathode agent at a later step becomes difficult.

For example, assuming that when an aqueous phosphoric acid solution is used as a counter electrode material, the 10 contact state of the solution with a dielectric film layer is complete and the capacitance appearance ratio (also called a cathode agent impregnation ratio) at the time is 100%, a capacitance appearance ratio of 100% can be hardly attained in the case of using a counter electrode material, having high viscosity, particularly a solid electrode 15 material. In particular, when the average particle size of tantalum powder is small or the sintered body manufactured from a tantalum powder has a large shape, the difficulty increases and in an extreme case, the capacitance 20 appearance ratio cannot reach even 50%. With such a low capacitance appearance ratio, the capacitor manufactured cannot have a sufficiently high moisture resistance.

In case the tantalum powder to produce a tantalum sintered body has a small pore diameter, it essentially 25 leads to a small pore diameter of the tantalum sintered body and a low capacitance appearance ratio. Consequently, a problem arises that an ESR cannot be lowered.

As one of means for solving these problems, a capacitor using a sintered body as an electrode may be considered, which sintered body is produced using an electrode material providing a dielectric material having a dielectric constant larger than that of tantalum and gives a high capacitance appearance ratio.

As such an electrode material which can be supplied industrially, niobium having a dielectric constant larger than that of tantalum and having a large reserve is known.

JP-A-55-157226 (the term "JP-A" as used herein means an "unexamined published Japanese patent application") discloses a method for producing a sintered device for capacitors, where agglomerated valve-acting metal powder having a particle size of 2.0 μm or less is molded under pressure and then sintered, the molded and sintered body is cut into fine pieces, a lead part is joined therewith and these are again sintered. However, the details on the producing method and properties of the niobium capacitor are not described in this patent publication.

U.S. Patent 4,084,965 discloses a capacitor using a sintered body of niobium powder having an average particle size of 5.1 μm obtained by hydrogenating and pulverizing a niobium ingot. However, the capacitor disclosed has a large leakage current (hereinafter sometimes simply referred to as "LC") value and is of little practical use.

JP-A-10-242004 (WO 98/38660) discloses a technique of partially nitriding a niobium powder and thereby improving

the LC value.

The tapping density of a niobium powder for a capacitor is an important factor in molding operation of the niobium powder. The tapping density of conventional 5 niobium powder is 2.5 g/ml or more, specifically about 4 g/ml, and this is insufficient for the molding.

That is, if such a niobium powder is molded and sintered to prepare a sintered body, the niobium powder poorly flows from the hopper of a molding machine to the 10 metal mold and it is difficult to weigh a constant amount of niobium powder and flow it into the metal mold. As a result, it causes problems such that the shape of the molded article is not satisfactorily stabilized, the molded article and the sintered body are deficient in the strength, 15 and a capacitor having bad LC is produced frequently. If a special molding apparatus capable of also handling a powder having bad flowability is used, the molding cost excessively increases and this is not practical.

As such, conventionally known niobium powder for 20 capacitors has a problem that the powder cannot be fully adapted to continuous molding and the productivity of capacitors is low.

DISCLOSURE OF THE INVENTION

25 The object of the present invention is to provide a capacitor having a large capacitance per unit mass, a small leakage current and a high moisture resistance; a sintered

body usable as the electrode material of this capacitor and capable of giving a high capacitance appearance ratio; a niobium powder being preferred as the material for this sintered body, exhibiting good flowability in the molding 5 operation, facilitating continuous molding and enabling stable production of capacitors; and the production methods of the capacitor, the sintered body and the niobium powder.

As a result of extensive investigations to solve the above-described problems, the present inventors have found 10 that when a niobium sintered body having a specific pore distribution, preferably having a plurality of pore diameter peak tops in the pore distribution is used for the capacitor electrode, a high capacitance appearance ratio can be obtained and a capacitor having small leakage current and good moisture resistance can be produced. The 15 present inventors also have found that a niobium powder preferably having a tapping density of 0.5 to 2.5 g/ml, more preferably having an average particle size of 10 to 1,000 μm exhibits good flowability, enables continuous 20 molding and is preferred as the material for the above-described sintered body and when this niobium powder is used, a capacitor having small leakage current can be stably produced. The present inventors have found that more 25 preferably, both a high capacitance appearance ratio and low ESR can be achieved with a capacitor wherein the electrodes use a niobium sintered body produced by using a niobium powder having a wide range of pore distribution and

a plural pore diameter peak tops all of which are 0.5 μm or more. The present invention has been accomplished based on these findings.

More specifically, the present invention relates to
5 the following niobium powder, niobium sintered body,
capacitor using thereof, and production methods of the
niobium powder, the niobium sintered body and the capacitor.

(1) A niobium powder for a capacitor having a tapping density of 0.5 to 2.5 g/ml.

10 (2) The niobium powder as described in 1 above,
wherein the average particle size is from 10 to 1,000 μm .

(3) The niobium powder as described in 1 or 2 above,
wherein the angle of repose is from 10° to 60°.

15 (4) The niobium powder as described in any one of 1
to 3 above, wherein the BET specific surface area is from
0.5 to 40 m^2/g .

(5) The niobium powder as described in any one of 1
to 4 above, which has a pore distribution having a pore
diameter peak top in the range of 0.01 μm to 500 μm .

20 (6) The niobium powder as described in 5 above,
wherein the pore distribution has a plurality of pore
diameter peak tops.

(7) The niobium powder as described in 5 or 6 above,
wherein any of the pore diameter peak tops is in the range
25 of 0.5 to 100 μm .

(8) The niobium powder as described in any one of 1
to 7 above, wherein at least one element selected from the

group consisting of nitrogen, carbon, boron and sulfur elements is contained in an amount of 200,000 mass ppm or less.

(9) A sintered body using the niobium powder
5 described in any one of 1 to 8 above.

(10) The sintered body as described in 9 above, which has a pore distribution having a pore diameter peak top in the range of 0.01 μm to 500 μm .

10 (11) A niobium sintered body for a capacitor electrode, wherein the pore distribution of the niobium sintered body has a plurality of pore diameter peak tops.

(12) The niobium sintered body as described in 11 above, wherein the pore distribution has two pore diameter peak tops.

15 (13) The niobium sintered body as described in 11 or 12 above, wherein among the plurality of pore diameter peak tops, the peak tops of the two peaks having a highest relative intensity are present in the range of 0.2 to 0.7 μm and in the range of 0.7 to 3 μm respectively.

20 (14) The niobium sintered body as described in any one of 11 to 13 above, wherein among the plurality of pore diameter peak tops, the peak top of the peak having a highest relative intensity is present in the larger diameter side than the peak top of the peak having a next highest relative intensity.

(15) The niobium sintered body as described in any one of 9 to 14 above, wherein the sintered body has a volume of

10 mm³ or more including the volume of pore void.

(16) The niobium sintered body as described in any one of 9 to 15 above, wherein the sintered body has a specific surface area of 0.2 to 7 m²/g.

5 (17) The niobium sintered body as described in any one of 9 to 16 above, wherein a part of the sintered body is nitrated.

10 (18) The niobium sintered body as described in any one of 12 to 17 above, wherein the sintered body is a sintered body obtained from a niobium molded article which gives a sintered body having a CV value of 40,000 to 200,000 µFV/g when sintered at 1,300°C.

15 (19) A capacitor comprising one electrode using the niobium sintered body described in any one of 9 to 18 above, a counter electrode and a dielectric material interposed therebetween.

(20) The capacitor as described in 19 above, wherein the dielectric material mainly comprises niobium oxide.

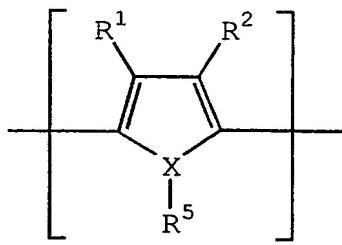
20 (21) The capacitor as described in 19 above, wherein the counter electrode is at least one material selected from the group consisting of an electrolytic solution, an organic semiconductor and an inorganic semiconductor.

25 (22) The capacitor as described in 21 above, wherein the counter electrode is an organic semiconductor and the organic semiconductor is at least one material selected from the group consisting of an organic semiconductor comprising a benzopyrroline tetramer and chloranile, an

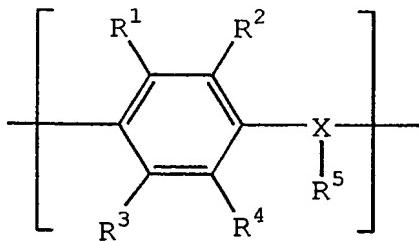
organic semiconductor mainly comprising tetrathiotetracene, an organic semiconductor mainly comprising tetracyanoquino-dimethane, and an electrically conducting polymer.

(23) The capacitor as described in 22 above, wherein
5 the electrically conducting polymer is at least one member selected from the group consisting of polypyrrole, polythiophene, polyaniline and substitution derivatives thereof.

(24) The capacitor as described in 22 above, wherein
10 the electrically conducting polymer is an electrically conducting polymer obtained by doping a dopant into a polymer containing a repeating unit represented by the following formula (1) or (2):



(1)

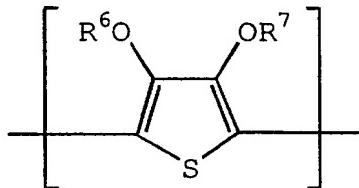


(2)

15 (wherein R¹ to R⁴ each independently represents a monovalent group selected from the group consisting of a hydrogen atom, a linear or branched, saturated or unsaturated alkyl, alkoxy or alkylester group having from 1 to 10 carbon atoms, a halogen atom, a nitro group, a cyano group, a primary,
20 secondary or tertiary amino group, a CF₃ group, a phenyl group and a substituted phenyl group; each of the pairs of R¹ and R², and R³ and R⁴ may combine at an arbitrary position

to form a divalent chain for forming at least one 3-, 4-, 5-, 6- or 7-membered saturated or unsaturated hydrocarbon cyclic structure together with the carbon atoms substituted by R¹ and R² or by R³ and R⁴; the cyclic combined chain may 5 contain a bond of carbonyl, ether, ester, amide, sulfide, sulfinyl, sulfonyl or imino at an arbitrary position; X represents an oxygen atom, a sulfur atom or a nitrogen atom; R⁵ is present only when X is a nitrogen atom, and independently represents a hydrogen atom or a linear or 10 branched, saturated or unsaturated alkyl group having from 1 to 10 carbon atoms).

(25) The capacitor as described in 24 above, wherein the electrically conducting polymer is an electrically conducting polymer containing a repeating unit represented, 15 by the following formula (3):



(3)

(wherein R⁶ and R⁷ each independently represents a hydrogen atom, a linear or branched, saturated or unsaturated alkyl group having from 1 to 6 carbon atoms, or a substituent for 20 forming at least one 5-, 6- or 7-membered saturated hydrocarbon cyclic structure containing two oxygen elements resulting from the alkyl groups combining with each other at an arbitrary position; and the cyclic structure includes a structure having a vinylene bond which may be substituted,

and a phenylene structure which may be substituted).

(26) The capacitor as described in 22 above, wherein the electrically conducting polymer is an electrically conducting polymer obtained by doping a dopant into 5 poly(3,4-ethylenedioxythiophene).

(27) The capacitor as described in 19 above, wherein the counter electrode is formed of a material at least partially having a layer structure.

10 (28) The capacitor as described in 19 above, wherein the material of the counter electrode contains an organic sulfonate anion as a dopant.

(29) A method for producing the niobium powder described in any one of 1 to 8 above, comprising activation-treatment of niobium or a niobium compound.

15 (30) The method for producing the niobium powder as described in 29 above, wherein the activation treatment of niobium or a niobium compound is performed by at least one step selected from the group consisting of a sintering step and a cracking step.

20 (31) The method for producing the niobium powder as described in 29 or 30 above, wherein the activation treatment of niobium or a niobium compound is performed using a mixture of niobium or a niobium compound and an activator.

25 (32) The method for producing the niobium powder as described in any one of 29 to 31 above, wherein the average particle size of the niobium or niobium compound processed

with the activation treatment is from 0.01 µm to 10 µm.

(33) The method for producing the niobium powder as described in any one of 29 to 32 above, wherein the niobium or niobium compound contains at least one element selected 5 from the group consisting of nitrogen, carbon, boron and sulfur in an amount of 200,000 ppm or less.

(34) The method for producing the niobium powder as described in any one of 29 to 33 above, wherein the niobium compound is at least one member selected from the group 10 consisting of niobium hydride, niobium alloy and niobium hydride alloy.

(35) The method for producing the niobium powder as described in 34 above, wherein the component other than niobium contained in the niobium alloy or niobium hydride ; 15 alloy is at least one element selected from the group consisting of elements having an atomic number of 88 or less excluding hydrogen, nitrogen, oxygen, fluorine, chlorine, bromine, iodine, niobium, helium, neon, argon, krypton, xenon and radon.

20 (36) The method for producing the niobium powder as described in 31 above, wherein the mixture containing niobium or a niobium compound and an activator is obtained by mixing these using a solvent.

25 (37) The method for producing the niobium powder as described in 36 above, wherein the solvent is at least one solvent selected from the group consisting of water, alcohols, ethers, cellosolves, ketones, aliphatic

hydrocarbons, aromatic hydrocarbons and halogenated hydrocarbons.

(38) The method for producing the niobium powder as described in 31 above, wherein the activator is used in an 5 amount of 1 to 40 mass% based on the total amount of the niobium or niobium compound.

(39) The method for producing the niobium powder as described in 31 or 38 above, wherein the average particle size of the activator is from 0.01 µm to 500 µm.

10 (40) The method for producing the niobium powder as described in any one of 31, 38 and 39 above, wherein the activator has a plurality of particle size peak tops.

15 (41) The method for producing the niobium powder as described in any one of 31 or 38 to 40 above, wherein the activator is a substance which is removed as a gas at 2,000°C or less.

20 (42) The method for producing the niobium powder as described in 41 above, wherein the activator is at least one member selected from the group consisting of naphthalene, anthracene, quinone, camphor, polyacrylic acid, polyacrylic acid ester, polyacrylamide, polymethacrylic acid, polymethacrylic acid ester, polymethacrylamide, polyvinyl alcohol, NH₄Cl, ZnO, WO₂, SnO₂ and MnO₃.

25 (43) The method for producing the niobium powder as described in any one of 31 or 38 to 40 above, wherein the activator is at least one member selected from the group consisting of a water-soluble substance, an organic

solvent-soluble substance, an acidic solution-soluble substance, an alkaline solution-soluble substance, a substance which forms a complex and becomes a substance soluble in water, organic solvent, acidic solution or
5 alkaline solution, and a substance which becomes a substance soluble in water, organic solvent, acidic solution or alkaline solution at 2,000°C or less.

(44) The method for producing the niobium powder as described in 43 above, wherein the activator is at least
10 one member selected from the group consisting of compounds of a metal with carbonic acid, sulfuric acid, sulfurous acid, halogen, perhalogen acid, hypohalogen acid, nitric acid, nitrous acid, phosphoric acid, acetic acid, oxalic acid or boric acid, metals, metal hydroxides and metal
15 oxides.

(45) The method for producing the niobium powder as described in 43 above, wherein the activator is at least one member selected from the group consisting of lithium, sodium, potassium, rubidium, cesium, francium, beryllium,
20 magnesium, calcium, strontium, barium, radium, scandium, yttrium, cerium, neodymium, titanium, zirconium, hafnium, vanadium, niobium, tantalum, molybdenum, tungsten, manganese, rhenium, ruthenium, osmium, cobalt, rhodium, iridium, nickel, palladium, platinum, silver, gold, zinc,
25 cadmium, boron, aluminum, gallium, indium, thallium, silicon, germanium, tin, lead, arsenic, antimony, bismuth, selenium, tellurium, polonium and compounds thereof.

(46) The method for producing the niobium powder as described in any one of 29 to 40 and 43 to 45 above, wherein the activation treatment is a treatment of removing the activator by heating and/or under reduced pressure 5 before or during the sintering step.

(47) The method for producing the niobium powder as described in any one of 29 to 40 and 43 to 45 above, wherein the activation treatment is a treatment of removing the activator component by contacting a solvent with the 10 sintered or cracked product after the sintering step and during or after the cracking step.

(48) The method for producing the niobium powder as described in 47 above, wherein the solvent is at least one member selected from the group consisting of water, an 15 organic solvent, an acidic solution, an alkaline solution and a solution containing a ligand of forming a soluble complex.

(49) The method for producing the niobium powder as described in 48 above, wherein the acidic solution is a 20 solution of at least one member selected from the group consisting of nitric acid, sulfuric acid, hydrofluoric acid and hydrochloric acid.

(50) The method for producing the niobium powder as described in 48 above, wherein the alkaline solution 25 contains at least one member selected from the group consisting of an alkali metal hydroxide and ammonia.

(51) The method for producing the niobium powder as

described in 48 above, wherein the ligand is at least one member selected from the group consisting of ammonia, glycine and ethylenediaminetetraacetic acid.

(52) The method for producing the niobium powder as described in 48 above, wherein the organic solvent is methyl isobutyl ketone.

(53) A method for producing a nitrogen-containing niobium powder, comprising treating the niobium powder described in any one of 1 to 7 above by at least one method selected from the group consisting of liquid nitridation, ion nitridation and gas nitridation.

(54) A method for producing a carbon-containing niobium powder, comprising treating the niobium powder described in any one of 1 to 7 above by at least one method selected from the group consisting of solid phase carbonization and liquid carbonization.

(55) A method for producing a boron-containing niobium powder, comprising treating the niobium powder described in any one of 1 to 7 above by at least one method selected from the group consisting of gas boronization and solid phase boronization.

(56) A method for producing a sulfur-containing niobium powder, comprising treating the niobium powder described in 1 or 7 above by at least one method selected from the group consisting of gas sulfidization, ion sulfidization and solid phase sulfidization.

(57) A niobium powder obtained by the production

method described in any one of 29 to 56 above.

(58) A method for producing a niobium sintered body, using the niobium powder described in any one of 1 to 8 and 57 above.

5 (59) A method for producing a capacitor comprising one electrode using a niobium sintered body, a dielectric material formed on the surface of the sintered body and a counter electrode provided on the dielectric material, wherein the niobium sintered body is obtained by sintering
10 the niobium powder described in any one of 1 to 8 and 57 above.

(60) The method for producing a capacitor as described in 59 above, wherein the dielectric material is formed by electrolytic oxidation.

15 (61) A method for producing a capacitor comprising one electrode using a niobium sintered body, a dielectric material formed on the surface of the sintered body and a counter electrode provided on the dielectric material, wherein the niobium sintered body is the niobium sintered
20 body described in any one of 9 to 18 above.

(62) An electronic circuit using the capacitor described in any one of 19 to 28 above.

(63) An electronic instrument using the capacitor described in any one of 19 to 28 above.

25

BRIEF DESCRIPTION OF DRAWINGS

Figure 1 is an enlarged view schematically

illustrating the niobium powder of the present invention which has two or more pore diameter peaks.

Figure 2 is an outline of a pore distribution of the niobium powder measured by a method of mercury penetration.

5

MODE FOR CARRYING OUT THE INVENTION

The capacitor having good leakage current characteristics and excellent moisture resistance, the niobium sintered body which enables these properties and 10 giving a high capacitance appearance ratio, the niobium powder preferred as a material for the sintered body, having good flowability and capable of continuous molding, and the production methods of the capacitor, the niobium sintered body and the niobium powder are described below.

15 In the present invention, a niobium powder for capacitors (sometimes simply referred to as a "niobium powder") having a tapping density of 0.5 to 2.5 g/ml is used as the niobium powder which satisfies the above-described properties of a capacitor and improves the 20 productivity in the production of capacitors.

The niobium powder for capacitors as used herein means a niobium powder mainly comprising niobium and capable of being a material for producing a capacitor. This niobium powder may contain, for example, a component capable of 25 forming an alloy with niobium, namely, a component other than niobium such as nitrogen and/or oxygen.

A capacitor can be produced by molding and sintering

the niobium powder for capacitors using a method as follows to obtain a niobium sintered body for capacitors (sometimes simply referred to as a niobium sintered body) followed by forming a dielectric layer and a counter electrode thereon.

5 The niobium powder for capacitors is added to a solution obtained by dissolving a binder which is described later, in an organic solvent such as toluene or methanol, and thoroughly mixed using a shaking mixer or a V-type mixer. Then, the organic solvent is distilled off under
10 reduced pressure using a drier such as conical drier to prepare a niobium mixed powder containing the binder. This mixed powder is charged into the hopper of an automatic molding machine, weighed while flowing the niobium powder through an inlet tube from the hopper to the metal mold of
15 the molding machine to automatically cause spontaneous falling in the metal mold, and molded together with a lead wire. After removing the binder, this molded article is sintered at 500 to 2,000°C under reduced pressure to manufacture a niobium sintered body.

20 The niobium sintered body is electrochemically formed, for example, in a electrolyte solvent such as phosphoric acid and adipic acid of a concentration of 0.1 % by mass and 30°C to 90°C at a voltage from 20 to 60 V for 1 to 30 hours to form a dielectric layer mainly comprising a
25 niobium oxide. A solid electrolyte layer such as manganese dioxide, lead dioxide and conductive polymer and a graphite layer and a silver paste layer are formed on the dielectric

layer. After a cathode terminal is connected thereon by soldering, these are sealed with a resin to fabricate a solid electrolyte capacitor.

In the case of a mixed powder having no appropriate flowability or angle of repose in molding, the powder does not smoothly flow from the hopper to the metal mold and the molding cannot be stably performed. In particular, since the mixed powder is transported from the hopper using a method such as vibration, too large or too small tapping density or average particle size of the mixed powder leads to large dispersion in the mass of the molded article or in the strength or shape of the sintered body and in some cases, to the generation of chipping or cracking, resulting in a bad leakage current value. Thus, the tapping density, the average particle size, the flowability and the angle of repose of the mixed powder are important factors for producing a good sintered body and a good capacitor.

These physical properties of the mixed powder scarcely change between before and after the mixing with a binder but are determined by the physical properties of the niobium powder for capacitors used. Accordingly, important are the tapping density, the average particle size, the flowability and the angle of repose of the niobium powder used. The flowability and the angle of repose of the niobium powder are greatly affected by the tapping density or the average particle size and therefore, the tapping density and the average particle size become important

factors.

In the present invention, for increasing the productivity and the strength of the sintered body accompanying the improvement of the flowability or the angle of repose and thereby obtaining an effect of reducing the leakage current, the tapping density is preferably from 0.5 to 2.5 g/ml, more preferably from 0.8 to 1.9 g/ml. The average particle size of the niobium powder of the present invention is preferably from 10 to 1,000 μm , more preferably from 50 to 200 μm .

For allowing the niobium powder to spontaneously fall from the hopper to the metal mold of a molding machine, the angle of repose of the niobium powder of the present invention is preferably from 10° to 60°, more preferably from 10° to 50°.

The niobium powder having the above-described physical properties can be produced starting from a mixture (hereinafter referred to as "a starting material mixture") containing a niobium powder or a niobium compound powder (hereinafter these are called "a starting material niobium powder") and an activator (also called "pore forming material", and hereinafter sometimes referred to as "an additive") through at least a sintering step and a cracking step in sequence.

The activator is removed at either the sintering step or the cracking step during the production of the niobium powder of the present invention from the starting material

mixture. The removal of the activator may also be performed independently from the sintering step or the cracking step.

Various methods for removing the activator can be arbitrarily employed according to the chemical properties 5 of the activator. One of the methods capable of easily removing the activator may be used or a plurality of these methods may be used in combination.

Examples of the method for removing the activator include a method of evaporating, sublimating or thermally 10 decomposing the activator and removing it as a gas, and a method of removing the activator by dissolving it in a solvent.

In the case of removing the activator as a gas, the removal may be performed at the sintering step, or a step 15 of removing the activator under heating and/or reduced pressure may be provided before the sintering.

In the case of removing the activator by dissolving it in a solvent after the sintering of the starting material mixture or during or after the cracking, a solvent which is 20 described later is contacted with the sintered product or a cracked product thereby dissolving and removing the activator.

A step of nitriding, boronizing, carbonizing or sulfidizing a part of niobium powder may be provided at any 25 stage in the process of producing the niobium powder of the present invention from the starting material mixture.

The method for producing the niobium powder of the

present invention is described in detail below.

The starting material niobium powder may be at least one powder selected from niobium, niobium hydride, niobium alloy and niobium hydride alloy. A part of the powder may 5 be nitrided, sulfidized, carbonized or boronized. The "alloy" as used in the present invention includes a solid solution with other alloy component.

The average particle size of the starting material niobium powder is preferably from 0.01 to 10 μm , more 10 preferably 0.02 to 5 μm , still more preferably from 0.05 to 2 μm .

Examples of the method for obtaining niobium used as the starting material niobium powder include a method of hydrogenating, pulverizing and dehydrogenating a niobium 15 ingot, a niobium pellet or a niobium powder, a method of reducing potassium fluoroniobate with sodium or the like and pulverizing the reduction product, a method of reducing niobium oxide using at least one of hydrogen, carbon, magnesium and aluminum and pulverizing the reduction 20 product, and a method of hydrogen-reducing niobium halide.

Examples of the method for obtaining niobium hydride used as the starting material niobium powder include a method of hydrogenating and pulverizing a niobium ingot, a niobium pellet or a niobium powder.

25 Examples of the method for obtaining a niobium hydride alloy used as the starting material niobium powder include a method of pulverizing a hydride of niobium alloy ingot,

niobium alloy pellet or niobium alloy powder. Examples of the method for obtaining a niobium alloy used as the starting material niobium powder include a method of dehydrogenating a niobium hydride alloy obtained as above.

5 The niobium alloy or niobium hydride alloy contains, as an alloy component other than niobium, at least one element selected from the group consisting of the elements having an atomic number of 88 or less excluding hydrogen, nitrogen, oxygen, fluorine, chlorine, bromine, iodine,
10 niobium, helium, neon, krypton, argon, xenon and radon.

The activator is a substance which can be removed at any step during the production of the niobium powder of the present invention from the starting material mixture. In the niobium powder of the present invention, a pore is
15 usually formed in the portion where the activator is removed.

The particle size of the activator affects the pore diameter of the niobium powder of the present invention, the pore diameter of the niobium powder affects the pore
20 diameter of the niobium sintered body, and the pore diameter of the niobium sintered body affects the capacitance of a capacitor and the impregnating ability of a cathode agent in the production step of a capacitor.

The impregnating ability of a cathode agent has a
25 great influence in producing a capacitor with a high capacitance as well as a low ESR. As a niobium sintered body is produced by molding a niobium powder under pressure,

the pore diameter of the niobium sintered body is naturally smaller than that of the niobium powder. Considering the difficulty to impregnate a cathode agent to a niobium sintered body produced from a niobium powder having a small 5 pore diameter, the average pore diameter of a niobium powder is preferably 0.5 μm or more, and more preferably 1 μm or more.

The average pore diameter of the niobium powder is preferably from 0.01 to 500 μm , more preferably from 0.03 10 to 300 μm , still more preferably from 0.1 to 200 μm . For having a pore diameter in this range, the average particle size of the activator is preferably from 0.01 to 500 μm , more preferably from 0.03 to 300 μm , still more preferably from 0.1 to 200 μm .

15 The average pore diameter of the niobium powder is most preferably from 0.5 μm to 100 μm , and the average particle size of the activator is most preferably from 0.5 to 100 μm .

The pore diameter may be reduced by using an activator 20 having a small particle size and the pore diameter may be increased by using an activator having a large particle size.

The pore diameter distribution can be adjusted by adjusting the particle size distribution of the activator.

25 In order to obtain a capacitor having a sufficiently large capacitance and free from problems involved in the impregnating ability of a cathode agent, it is preferred to

appropriately provide pores small enough to give a desired capacitance and pores large enough to ensure satisfactory impregnation of a cathode agent, in the niobium sintered body according to the physical properties of the cathode agent.

For adjusting the pore diameter distribution of the niobium powder or niobium sintered body, for example, the niobium powder can be made to have a pore diameter distribution having two or more peak tops by using an activator (powder) with a particle size distribution with two or more peak tops. By sintering this niobium powder, a niobium sintered body having two or more peak tops of equal pore diameter in the pore diameter distribution can be obtained. In this case, the pore diameter peak top is, preferably present in the range of 0.01 to 500 μm , more preferably from 0.03 to 300 μm , still more preferably from 0.1 to 200 μm , particularly preferably from 0.1 to 30 μm and most preferably from 0.2 to 3 μm .

The niobium powder to produce the niobium sintered body in above has a two or more peak tops in the particle size distribution. Any of the two or more peak tops is preferably 0.5 μm or more. For example, to produce a niobium sintered body having two peak tops in the particle size distribution of 0.7 and 3 μm , the two peak tops of the niobium powder may be adjusted to about 1.5 and about 25 μm . To obtain a niobium powder having a small pore diameter of 1.5 μm and having a large pore diameter of 25 μm , the

activator having an average pore diameter of 1.5 μm and 25 μm is to be used respectively. Generally, when a pore of a small diameter and that of a large diameter are present in the niobium powder, a large diameter becomes small during 5 molding under pressure. Therefore, a peak top of a large diameter is preferably 20 μm or more. Also, preferably 30% by volume or more of the entire pore volume has a pore diameter of 20 μm or more, and more preferably 40% by volume or more.

10 The above example is herein described with details based on drawings. Figure 1 is an enlarged view schematically illustrating the niobium powder of the present invention. The niobium powder in Figure 1 is a granulated powder comprising a primary powder which has a specific pore diameter formed by an activator. Pores (A) and (B) are formed by using an activator having an average diameter of about 1.5 μm and about 25 μm respectively. Thus, it is possible to coagulate a primary powder to each other efficiently. Figure 2 is an outline of a pore distribution 15 of the niobium powder measured by a method of mercury penetration. Peak (A) is the peak corresponding to pore (A) formed by the activator having an average diameter of about 1.5 μm and peak (B) is the peak corresponding to pore (B) formed by the activator having an average diameter of about 20 μm respectively. Peak (B) is higher than peak (A) and 20 44 % of the entire pore volume has a pore diameter of 20 μm or more.

The activator having two or more peak tops in the particle size distribution can be obtained, for example, by mixing two or more activators having a different peak top in the particle size distribution.

5 Examples of the substance as the activator include a substance which becomes a gas at the sintering temperature or lower, and a substance which is soluble in a solvent at least after the sintering.

Examples of the substance which becomes a gas at the
10 sintering temperature or lower include a substance which becomes a gas through evaporation, sublimation or thermal decomposition. An inexpensive substance capable of easily becoming a gas even at a low temperature without leaving a residue is preferred. Examples thereof include aromatic
15 compounds such as naphthalene, anthracene and quinone, camphor, NH₄Cl, ZnO, WO₂, SnO₂, MnO₃ and organic polymers.

Examples of the organic polymer include polyacrylic acid, polyacrylic acid ester, polyacrylamide, polymethacrylic acid, polymethacrylic acid ester,
20 polymethacrylamide and polyvinyl alcohol.

The substance which is soluble at least after the sintering is a substance such that the residue of the activator or a thermally decomposed product thereof is soluble in a solvent. A substance capable of easily
25 dissolving in a solvent which is described later, after the sintering, or during or after the cracking is particularly preferred. Such a substance can be selected from many

substances according to the combination with the solvent.

Examples thereof include compounds of a metal with carbonic acid, sulfuric acid, sulfurous acid, halogen, perhalogen acid, hypohalogen acid, nitric acid, nitrous acid, phosphoric acid, acetic acid, oxalic acid or boric acid, metal oxides, metal hydroxides and metals.

Among these, preferred are compounds having a large solubility in a solvent such as acid, alkali or ammonium salt solution which are described later. Examples thereof include compounds containing at least one member selected from the group consisting of lithium, sodium, potassium, rubidium, cesium, francium, beryllium, magnesium, calcium, strontium, barium, radium, scandium, yttrium, cerium, neodymium, erbium, titanium, zirconium, hafnium, vanadium, niobium, tantalum, molybdenum, tungsten, manganese, rhenium, ruthenium, osmium, cobalt, rhodium, iridium, nickel, palladium, platinum, silver, gold, zinc, cadmium, aluminum, gallium, indium, thallium, germanium, tin, lead, antimony, bismuth, selenium, tellurium, polonium, boron, silicon and arsenic. Among these, preferred are metal salts and more preferred are, for example, barium oxide, manganese(II) nitrate and calcium carbonate.

These activators may be used individually or in combination of two or more thereof.

To form a specific pore diameter efficiently, a substance which exists as a solid at a sintering temperature is preferable as the material of the activator.

The reason is that the activator being present in a solid state at a sintering temperature blocks excessive agglomeration of the primary niobium powder and allows the fusion of the niobium powder only at a contact point to 5 each other. If the activator exists as a liquid or gas at a sintering temperature, it has a small effect to block such agglomeration and may form a smaller pore than desired. Consequently, a pore diameter becomes more stable with an activator comprising a substance of a higher melting point 10 such as barium oxide, calcium carbonate, aluminum oxide and magnesium oxide than an activator comprising a substance of a lower melting point such as an aluminum metal, magnesium metal, magnesium hydride and calcium metal.

If the activator is added in a small amount, the 15 tapping density and the angle of repose become large, whereas if added in a large amount, the tapping density becomes small and closed pores increase at the stage of sintering. For obtaining a repose angle of 60° or less and a tapping density of 0.5 to 2.5 g/ml without the problem of 20 closed pores at the sintering stage, the amount of the activator added is generally from 1 to 40 mass% or less (unless otherwise indicated, mass% is hereinafter simply referred to as %), preferably from 5 to 25%, more preferably from 10 to 20%, based on the starting material 25 niobium, though this varies depending on the average particle size of the activator.

The starting material mixture may be obtained by

mixing the activator and the niobium starting material each in the powder form using no solvent or by mixing the activator and the niobium starting material using an appropriate solvent and drying the mixture.

5 Examples of the solvent which can be used include water, alcohols, ethers, cellosolves, ketones, aliphatic hydrocarbons, aromatic hydrocarbons and halogenated hydrocarbons.

The mixing may be performed using a mixer. As for the
10 mixer, a normal apparatus such as shaking mixer, V-type mixer and Nauter mixer may be used without any problem. The temperature at the mixing is limited by the boiling point and freezing point of the solvent but is generally from -50°C to 120°C, preferably from -50°C to 50°C, more
15 preferably from -10°C to 30°C. The time spent for the mixing is not particularly limited insofar as it is 10 minutes or more, however, the mixing is generally performed for 1 to 6 hours preferably in an oxygen-free atmosphere using an inert gas such as nitrogen or argon.

20 In the case of using a solvent, the mixture obtained is dried at lower than 80°C, preferably lower than 50°C, using a conical drier or a compartment drier. If the mixture is dried at a temperature of 80°C or higher, the oxygen contained in the niobium or niobium hydride powder
25 disadvantageously increases.

In the case where the activator becomes a gas at the sintering temperature or lower, the activator may be

removed at the sintering but a step of forming the activator into a gas and removing it before the sintering may be independently provided by setting the conditions such as temperature, pressure and time period to those of 5 facilitating the removal according to the chemical properties of the activator. In this case, the activator is vaporized, for example, at 100°C to 800°C under reduced pressure within a few hours.

In the case of using a niobium hydride or a niobium 10 hydride alloy as the starting material niobium, the dehydrogenation can be attained irrespective of the kind of the activator by performing the above-described step.

The sintering step is performed at 500°C to 2,000°C, preferably from 800°C to 1,500°C, more preferably from 15 1,000°C to 1,300°C, under reduced pressure or in a reducing atmosphere such as argon. After the completion of sintering, the sintered product is preferably cooled until the niobium temperature (sometimes simply referred to as a "product temperature") becomes 30°C or less, an inert gas such as 20 nitrogen or argon containing from 0.01 vol% to 10 vol%, preferably from 0.1 vol% to 1 vol% of oxygen is gradually added such that the product temperature does not exceed 30°C, and after standing for 8 hours or more, the sintered product is taken out to obtain a sintered lump.

25 In the cracking step, the sintered lump is cracked to an appropriate particle size using a cracking machine such as a roll granulator.

In the case where the activator is soluble in a solvent at least after the sintering step, an appropriate solvent is contacted with the sintered lump or the cracked powder after the sintering and before, during or after the cracking or at a plurality of these steps and thereby, the activator component is dissolved and removed. In view of easiness of the removal, the activator component is preferably dissolved and removed from the cracked powder after cracking.

The solvent used here is a solvent in which the activator to be dissolved has a sufficiently high solubility. A solvent which is inexpensive and hardly remains is preferred. For example, in the case of a water-soluble activator, water may be used; in the case of an organic solvent-soluble activator, an organic solvent such as methyl isobutyl ketone, ethanol or dimethyl sulfoxide (DMSO) may be used; in the case of an acid-soluble activator, an acid solution such as nitric acid, sulfuric acid, phosphoric acid, boric acid, carbonic acid, hydrofluoric acid, hydrochloric acid, hydrobromic acid, hydroiodic acid or organic acid may be used; in the case of an alkali-soluble activator, an alkali solution such as hydroxide of alkali metal, hydroxide of alkaline earth metal or ammonia may be used; and in the case of an activator which forms a soluble complex, a solution of an amine such as ammonia or ethylenediamine, an amino-acid such as glycine, a polyphosphoric acid such as sodium

tripolyphosphate, a crown ether, a thiosulfate such as sodium thiosulfate, or a chelating agent such as ethylenediaminetetraacetic acid, which becomes a ligand of the complex, may be used.

5 A solution of an ammonium salt such as ammonium chloride, ammonium nitrate and ammonium sulfate, cation exchange resin and anion exchange resin may also be used suitably. It is preferable to dissolve and remove the activator at a lower temperature. If the activator is
10 dissolved and removed at a high temperature, the surface of a niobium becomes oxidized because a niobium has a high affinity with oxygen. Consequently, a temperature of dissolving and removing is preferably 50°C or lower, more preferably from -10 °C to 40 °C and still more preferably,
15 from 0 °C to 30 °C. According to the above reason, it is preferable to select a method generating little heat in dissolving and removing. For example, when using a metal oxide or metal as an activator, dissolving and removing by an acid generally yields a high heat of neutralization.
20 Therefore, it is preferable to select a method which generates little heat such as dissolving in water and an organic solvent, forming a soluble complex such by using a solvent of ammonium nitrate salt, and ethylenediaminetetraacetate and dissolving in a solvent
25 containing ion exchange resin.

Specific examples of the combination of an activator and a solvent include barium oxide and water, calcium

oxalate and hydrochloric acid, aluminum oxide and aqueous sodium hydroxide solution, hafnium oxide and methyl isobutyl ketone, and magnesium carbonate and aqueous tetrasodium ethylenediaminetetraacetate solution.

5 After dissolving and removing the activator, the residue is thoroughly washed and dried. For example, in the case where barium oxide is removed with water, the residue is thoroughly washed using an ion-exchanged solution until the electric conductivity of the washing solution is
10 reduced to 5 $\mu\text{S}/\text{cm}$ or less. Subsequently, the product is dried at a product temperature of 50°C or less under reduced pressure. Here, the amount of the remaining activator or solvent component is usually 100 ppm or less, though this varies depending on the washing conditions.

15 In order to improve the LC value, the thus-obtained niobium powder, sintered lump and niobium starting material powder may be subjected to nitridation, boronization, carbonization or sulfidization of a part of the niobium powder, or to a plurality of these treatments.

20 The niobium powder of the present invention may contain the obtained niobium nitride, niobium boride, niobium carbide or niobium sulfide or a plurality of these species. The total content of respective elements of nitrogen, boron, carbon and sulfur varies depending on the
25 shape of the niobium powder, however, it is from 0 to 200,000 ppm, preferably 50 to 100,000 ppm, more preferably 200 to 20,000 ppm. If the total content exceeds 200,000 ppm,

the capacitor produced is deteriorated in the capacitance characteristics and not suitable as a capacitor.

The nitridation of the niobium powder can be performed by any one of liquid nitridation, ion nitridation and gas 5 nitridation or by a combination thereof. Among these, gas nitridation in a nitrogen gas atmosphere is preferred because the apparatus therefor is simple and the operation is easy. For example, the gas nitridation in a nitrogen gas atmosphere can be attained by allowing the above-described 10 niobium powder to stand in a nitrogen gas atmosphere. With a nitridation atmosphere temperature of 2,000°C or less and a standing time of 100 hours or less, a niobium powder having an objective nitrided amount can be obtained. The treatment time can be shortened by performing the treatment, 15 at a higher temperature.

The boronization of the niobium powder may be either gas boronization or solid phase boronization. For example, the niobium powder may be boronized by allowing it to stand together with a boron source such as boron pellet or boron 20 halide (e.g., trifluoroboron), at 2,000°C or less for from 1 minute to 100 hours under reduced pressure.

The carbonization of the niobium powder may be any one of gas carbonization, solid phase carbonization and liquid carbonization. For example, the niobium powder may be 25 carbonized by allowing it to stand together with a carbon source—such as carbon material or organic material having carbon (e.g., methane), at 2,000°C or less for from 1 minute

to 100 hours under reduced pressure.

The sulfidization of the niobium powder may be any one of gas sulfidization, ion sulfidization and solid phase sulfidization. For example, the gas sulfidization in a sulfur gas atmosphere can be attained by allowing the niobium powder to stand in a sulfur atmosphere. With a sulfidization atmosphere temperature of 2,000°C or less and a standing time of 100 hours or less, a niobium powder having an objective sulfidized amount can be obtained. The treatment time can be shortened by performing the treatment at a higher temperature.

The BET specific surface area of the thus-obtained niobium powder of the present invention is usually 0.5 to 40 m²/g, preferably 0.7 to 10 m²/g, more preferably 0.9 to 2 m²/g.

The niobium powder of the present invention may be a mixture of niobium powders different in the tapping density, the particle size, the angle of repose, the BET specific surface area, the pore diameter distribution and the treatment by nitridation, boronization, carbonization or sulfidization.

The sintered body of the present invention, which can be used as an electrode for capacitors, is preferably produced, for example, by sintering the above-described niobium powder of the present invention. For example, the sintered body can be obtained by press-molding the niobium powder into a predetermined shape and then heating it at

from 500°C to 2,000°C, preferably from 800°C to 1,500°C, more preferably from 1,000°C to 1,300°C, for 1 minute to 10 hours under a pressure of 10^{-5} to 10^2 Pa.

The pore size distribution of the sintered body obtained from the niobium powder of the present invention usually has a pore diameter peak top in the range of 0.01 μm to 500 μm.

By adjusting the applied pressure at the molding to a specific pressure value, the sintered body can have a larger number of pore diameter peak tops than that of the niobium powder. This applied pressure value varies depending on the press-molding conditions such as physical properties of niobium powder, shape of a molded article and molding machine, but is in the range from a pressure capable of press-molding to a pressure where pores of the sintered body are not closed. The preferred pressure value can be determined by a preliminary experiment according to the conditions such as the physical properties of the niobium powder to be molded so as to have a plurality of pore size peak tops. The applied pressure value can be controlled, for example, by controlling the load of the molding machine applied on the molded article.

The pore size distribution of the sintered body preferably has at least two pore size peak tops so as to contain pores small enough to obtain a desired capacitance and pores large enough to ensure satisfactory impregnation of a cathode agent according to the physical properties of

the cathode agent. From such a sintered body having a plurality of peak tops in the pore diameter distribution, a capacitor having excellent impregnating ability of a counter electrode and a high capacitance appearance ratio 5 can be produced.

When among a plurality of pore diameter distribution peak tops, the peak tops of two peaks having a highest relative intensity are present in the range from 0.2 to 0.7 μm and in the range from 0.7 μm to 3 μm , respectively, 10 preferably from 0.2 μm to 0.7 μm and from 0.9 μm to 3 μm , respectively, the capacitor produced from this sintered body can have good moisture resistance. Among a plurality of the pore diameter distribution peak tops, the peak top 15 of the peak having a highest relative intensity is, preferably present in the larger diameter side than the peak top of the peak having a next highest relative intensity, because the capacitor can have more excellent moisture resistance.

The specific surface area of the thus-produced 20 sintered body is generally from 0.2 m^2/g to 7 m^2/g .

Usually, as the shape of the sintered body is larger, the impregnation of a counter electrode is more difficult. For example, in the case where the sintered body has a size of 10 mm^3 or more, the sintered body of the present 25 invention having a plurality of peak tops in the pore diameter distribution can be particularly effectively used.

The sintered body of the present invention may be

partially nitrided. As for the nitridation method, the method and reaction conditions described above with respect to the niobium powder can be employed. It is also possible to previously nitride a part of the niobium powder for use 5 of producing a sintered body and nitride a part of the sintered body produced from this niobium powder.

Such a sintered body usually contains from 500 to 70,000 mass ppm of oxygen, because natural oxidation oxygen contained in the niobium powder before the sintering and 10 oxygen added by the natural oxidation after the sintering are present. In the sintered body of the present invention, the content of elements except for niobium, alloy-forming element, oxygen and nitrogen is usually 400 mass ppm or less.

15 As one example, when the sintered body of the present invention is sintered at 1,300°C, the CV value (the product of the electrochemical forming voltage in the electrochemical forming at 80°C for 120 minutes in an aqueous 0.1 mass% phosphoric acid solution and the 20 capacitance at 120 Hz) is 40,000 to 200,000 µFV/g.

The production of a capacitor device is described below.

For example, a lead wire comprising a valve-acting metal such as niobium or tantalum and having appropriate 25 shape and length is prepared and this lead wire is integrally molded at the press-molding of the niobium powder such that a part of the lead wire is inserted into

the inside of the molded article, whereby the lead wire can work out to a leading line of the sintered body. Or, the niobium powder is molded and sintered without using a lead wire and then, a lead wire separately prepared is connected 5 thereto by welding or the like.

Using this sintered body as one electrode, a capacitor can be produced by interposing a dielectric material between this electrode and a counter electrode. For example, a capacitor is fabricated by using a niobium sintered body 10 as one electrode, forming a dielectric material on the surface of the sintered body (including the inside surface of pore) and providing a counter electrode on the dielectric material.

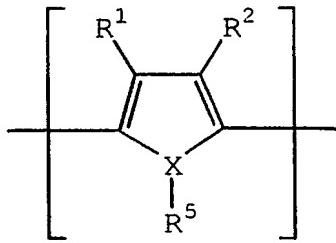
The dielectric material used here for the capacitor is 15 preferably a dielectric material mainly comprising niobium oxide, more preferably a dielectric material mainly comprising niobium pentaoxide. The dielectric material mainly comprising niobium pentaoxide can be obtained, for example, by electrolytically oxidizing the niobium sintered 20 body as one electrode. For electrolytically oxidizing the niobium electrode in an electrolytic solution, an aqueous protonic acid solution is generally used, such as aqueous 0.1% phosphoric acid solution, aqueous sulfuric acid solution, aqueous 1% acetic acid solution or aqueous adipic 25 acid solution. In the case of obtaining a niobium oxide dielectric material by electrochemically forming the niobium electrode in an electrolytic solution as such, the

capacitor of the present invention is an electrolytic capacitor and the niobium electrode serves as an anode.

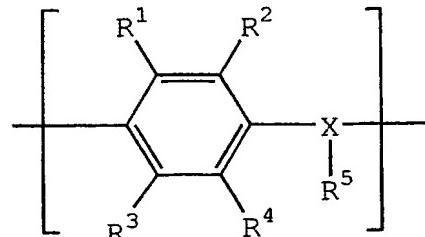
In the capacitor of the present invention, the counter electrode to the niobium sintered body is not particularly limited and for example, at least one material (compound) selected from electrolytic solutions, organic semiconductors and inorganic semiconductors known in the art of aluminum electrolytic capacitor, may be used.

Specific examples of the electrolytic solution include 10 a dimethylformamide-ethylene glycol mixed solution having dissolved therein 5 mass% of an isobutyltripropylammonium borotetrafluoride electrolyte, and a propylene carbonate-ethylene glycol mixed solution having dissolved therein 7 mass% of tetraethylammonium borotetrafluoride.

Specific examples of the organic semiconductor include 15 an organic semiconductor comprising benzene pyrroline tetramer and chloranile, an organic semiconductor mainly comprising tetrathiotetracene, an organic semiconductor mainly comprising tetracyanoquinodimethane, and an electrically conducting polymer containing a repeating unit 20 represented by the following formula (1) or (2):



(1)



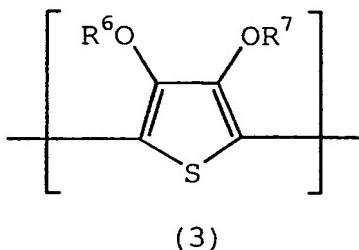
(2)

wherein R¹ to R⁴ each independently represents a monovalent group selected from the group consisting of a hydrogen atom, a linear or branched, saturated or unsaturated alkyl, alkoxy or alkylester group having from 1 to 10 carbon atoms,
5 a halogen atom, a nitro group, a cyano group, a primary, secondary or tertiary amino group, a CF₃ group, a phenyl group and a substituted phenyl group; each of the pairs of R¹ and R², and R³ and R⁴ may combine at an arbitrary position to form a divalent chain for forming at least one 3-, 4-,
10 5-, 6- or 7-membered saturated or unsaturated hydrocarbon cyclic structure together with the carbon atoms substituted by R¹ and R² or by R³ and R⁴; the cyclic combined chain may contain a bond of carbonyl, ether, ester, amide, sulfide, sulfinyl, sulfonyl or imino at an arbitrary position; X,
15 represents an oxygen atom, a sulfur atom or a nitrogen atom; R⁵ is present only when X is a nitrogen atom, and independently represents a hydrogen atom or a linear or branched, saturated or unsaturated alkyl group having from 1 to 10 carbon atoms.

20 In the present invention, R¹ to R⁴ in formula (1) or (2) each independently preferably represents a hydrogen atom or a linear or branched, saturated or unsaturated alkyl or alkoxy group having from 1 to 6 carbon atoms, and each of the pairs of R¹ and R², and R³ and R⁴ may combine to
25 form a ring.

In the present invention, the electrically conducting—
polymer containing a repeating unit represented by formula

(1) is preferably an electrically conducting polymer containing a structure unit represented by the following formula (3) as a repeating unit:



5 wherein R⁶ and R⁷ each independently represents a hydrogen atom, a linear or branched, saturated or unsaturated alkyl group having from 1 to 6 carbon atoms, or a substituent for forming at least one 5-, 6- or 7-membered saturated hydrocarbon cyclic structure containing two oxygen elements
10 resulting from the alkyl groups combining with each other at an arbitrary position; and the cyclic structure includes a structure having a vinylene bond which may be substituted, and a phenylene structure which may be substituted.

The electrically conducting polymer containing such a
15 chemical structure is doped with a dopant and for the dopant, known dopants can be used without limitation.

Specific examples of the inorganic semiconductor include an inorganic semiconductor mainly comprising lead dioxide or manganese dioxide, and an inorganic
20 semiconductor comprising triiron tetraoxide. These semiconductors may be used individually or in combination of two or more thereof.

Examples of the polymer containing a repeating unit represented by formula (1) or (2) include polyaniline,

polyoxyphenylene, polyphenylene sulfide, polythiophene, polyfuran, polypyrrole, polymethylpyrrole, and substitution derivatives and copolymers thereof. Among these, preferred are polypyrrole, polythiophene and substitution derivatives thereof (e.g., poly(3,4-ethylenedioxythiophene)).

When the organic or inorganic semiconductor used has an electrical conductivity of 10^{-2} S/cm to 10^3 S/cm, the capacitor produced can have a smaller impedance value and can be increased in the capacitance at a high frequency.

The electrically conducting polymer layer is produced, for example, by a method of polymerizing a polymerizable compound such as aniline, thiophene, furan, pyrrole, methylpyrrole or a substitution derivative thereof under the action of an oxidizing agent capable of satisfactorily undergoing an oxidation reaction of dehydrogenative two-electron oxidation. Examples of the polymerization reaction from the polymerizable compound (monomer) include vapor phase polymerization and solution polymerization. The electrically conducting polymer layer is formed on the surface of the niobium sintered body having thereon a dielectric material. In the case where the electrically conducting polymer is an organic solvent-soluble polymer capable of solution coating, a method of coating the polymer on the surface of the sintered body to form an electrically conducting polymer layer is used.

One preferred example of the production method using the solution polymerization is a method of dipping the

niobium sintered body having formed thereon a dielectric layer in a solution containing an oxidizing agent (Solution 1) and subsequently dipping the sintered body in a solution containing a monomer and a dopant (Solution 2), thereby 5 performing the polymerization to form an electrically conducting polymer layer on the surface of the sintered body. Also, the sintered body may be dipped in Solution 1 after it is dipped in Solution 2. Solution 2 used in the above-described method may be a monomer solution not 10 containing a dopant. In the case of using a dopant, the dopant may be allowed to be present together in the solution containing an oxidizing agent.

The operation of performing these polymerization steps is repeated once or more, preferably from 3 to 20 times, 15 per the niobium sintered body having thereon a dielectric material, whereby a dense and stratified electrically conducting polymer layer can be easily formed.

In the production method of a capacitor of the present invention, any oxidizing agent may be used insofar as it 20 does not adversely affect the capacitor performance and the reductant of the oxidizing agent can work out to a dopant and elevate the electrically conductivity of the electrically conducting polymer. An industrially inexpensive compound easy to handle at the production is 25 preferred.

Specific examples of the oxidizing agent include Fe(III)-base compounds such as FeCl_3 , FeClO_4 and Fe (organic

acid anion) salt; anhydrous aluminum chloride/cuprous chloride; alkali metal persulfates; ammonium persulfates; peroxides; manganesees such as potassium permanganate; quinines such as 2,3-dichloro-5,6-dicyano-1,4-benzoquinone 5 (DDQ), tetrachloro-1,4-benzoquinone and tetracyano-1,4-benzoquinone; halogens such as iodine and bromine; peracid; sulfonic acid such as sulfuric acid, fuming sulfuric acid, sulfur trioxide, chlorosulfuric acid, fluorosulfuric acid and amidosulfuric acid; ozone; and a mixture of a plurality 10 of these oxidizing agents.

Examples of the fundamental compound of the organic acid anion for forming the above-described Fe (organic acid anion) salt include organic sulfonic acid, organic carboxylic acid, organic phosphoric acid and organic boric acid. Specific examples of the organic sulfonic acid include benzenesulfonic acid, p-toluenesulfonic acid, methanesulfonic acid, ethanesulfonic acid, α -sulfo-naphthalene, β -sulfonaphthalene, naphthalenedisulfonic acid and alkynaphthalenesulfonic acid (examples of the alkyl group include butyl, triisopropyl and di-tert-butyl).

Specific examples of the organic carboxylic acid include acetic acid, propionic acid, benzoic acid and oxalic acid. Furthermore, polymer electrolyte anions such as polyacrylic acid, polymethacrylic acid, polystyrene-sulfonic acid, polyvinylsulfonic acid, poly- α -methylsulfonic acid, polyvinylsulfuric acid and polyethylenesulfonic acid and polyphosphoric acid may also

be used in the present invention. These organic sulfuric acids and organic carboxylic acids are mere examples and the present invention is not limited thereto. Examples of the counter cation to the above-described anion include
5 alkali metal ions such as H⁺, Na⁺ and K⁺, and ammonium ions substituted by a hydrogen atom, a tetramethyl group, a tetraethyl group, a tetrabutyl group or a tetraphenyl group, however, the present invention is not limited thereto. Among these oxidizing agents, preferred are oxidizing
10 agents containing a trivalent Fe-base compound, cuprous chloride, an alkali persulfate, an ammonium persulfate or a quinone.

For the anion having a dopant ability which is allowed
12 to be present together, if desired, in the production of
15 a polymer composition for the electrically conducting polymer (anion other than the reductant anion of the oxidizing agent), an electrolyte anion having as a counter anion an oxidizing agent anion (a reductant of oxidizing agent) produced from the above-described oxidizing agent,
20 or other electrolyte anion may be used. Specific examples thereof include protonic acid anions including halide anion of Group 5B elements such as PF₆⁻, SbF₆⁻ and AsF₆⁻; halide anion of Group 3B elements such as BF₄⁻; halogen anion such as I⁻(I₃⁻), Br⁻ and Cl⁻; perhalogenate anion such as ClO₄⁻;
25 Lewis acid anion such as AlCl₄⁻, FeCl₄⁻ and SnCl₅⁻; inorganic acid anion such as NO₃⁻ and SO₄²⁻; sulfonate anion such as p-toluenesulfonic acid, naphthalenesulfonic acid and alkyl-

substituted naphthalenesulfonic acid having from 1 to 5 carbon atoms (hereinafter simply referred to as "C1-5"); organic sulfonate anion such as CF_3SO_3^- and CH_3SO_3^- ; and carboxylate anion such as CH_3COO^- and $\text{C}_6\text{H}_5\text{COO}^-$.

5 Other examples include polymer electrolyte anions such as polyacrylic acid, polymethacrylic acid, polystyrene-sulfonic acid, polyvinylsulfonic acid, polyvinylsulfuric acid, poly- α -methylsulfonic acid, polyethylenesulfonic acid and polyphosphoric acid. However, the present invention is
10 not limited thereto. Among these anions, preferred is a high molecular or low molecular organic sulfonic acid compound or polyphosphoric acid compound. Preferably, an aromatic sulfonic acid compound (e.g., sodium dodecylbenzenesulfonate, sodium naphthalenesulfonate) is
15 used as the anion-donating compound.

Among the organic sulfonate anions, more effective dopants are a sulfoquinone compound having one or more sulfo-anion group ($-\text{SO}_3^-$) within the molecule and having a quinone structure, and an anthracene sulfonate anion.

20 Examples of the fundamental skeleton for the sulfoquinone anion of the above-described sulfoquinone compound include p-benzoquinone, o-benzoquinone, 1,2-naphthoquinone, 1,4-naphthoquinone, 2,6-naphthoquinone, 9,10-anthraquinone, 1,4-anthraquinone, 1,2-anthraquinone,
25 1,4-chrysenequinone, 5,6-chrysenequinone, 6,12-chrysenequinone, acenaphthoquinone, acenaphthenequinone, camphorquinone, 2,3-bornanedione, 9,10-phenanthrenequinone

and 2,7-pyrenequinone.

In the case where the counter electrode is solid, an electrically conducting layer may be provided thereon so as to attain good electrical contact with an exterior leading
5 line (for example, lead frame) which is used, if desired.

The electrically conducting layer can be formed, for example, by the solidification of an electrically conducting paste, the plating, the metallization or the formation of a heat-resistant electrically conducting resin
10 film. Preferred examples of the electrically conducting paste include silver paste, copper paste, aluminum paste, carbon paste and nickel paste, and these may be used individually or in combination of two or more thereof. In the case of using two or more kinds of pastes, the pastes
15 may be mixed or may be superposed one on another as separate layers. The electrically conducting paste applied is then solidified by allowing it to stand in air or under heating. Examples of the plating include nickel plating, copper plating, silver plating and aluminum plating.
20 Examples of the metal vapor-deposited include aluminum, nickel, copper and silver.

More specifically, for example, carbon paste and silver paste are stacked in this order on the second electrode and these are molded with a material such as
25 epoxy resin, thereby fabricating a capacitor. This capacitor may have a niobium or tantalum lead which is sintered and molded integrally with the niobium sintered

body or welded afterward.

The thus-fabricated capacitor of the present invention is jacketed using, for example, resin mold, resin case, metallic jacket case, dipping of resin or laminate film, 5 and then used as a capacitor product for various uses.

In the case where the counter electrode is liquid, the capacitor fabricated comprising the above-described two electrodes and a dielectric material is housed, for example, in a can electrically connected to the counter electrode to 10 complete the capacitor. In this case, the electrode side of the niobium sintered body is guided outside through a niobium or tantalum lead described above and at the same time, insulated from the can using an insulating rubber or the like.

15 By producing a sintered body for capacitors using the niobium powder produced according to the embodiment of the present invention described in the foregoing pages and producing a capacitor from the sintered body, a capacitor having a small leakage current and good reliability can be 20 obtained.

The capacitor of the present invention has a larger electrostatic capacitance for the volume than the conventional tantalum capacitors and therefore, a more compact capacitor product can be obtained.

25 The capacitor of the present invention having such properties can be applied to uses, for example, as a bypass capacitor or a coupling capacitor which are frequently

used in an analogue circuit and a digital circuit, and also to uses of conventional tantalum capacitors.

In general, such a capacitor is frequently used in an electronic circuit and when the capacitor of the present invention is used, the limitation in the arrangement of electronic parts or the discharge of heat can be relieved, as a result, an electronic circuit having high reliability can be disposed in a narrower space than that necessary for conventional electronic circuits.

Furthermore, when the capacitor of the present invention is used, an electronic instrument having smaller size and higher reliability than conventional ones can be obtained, such as a computer, computer peripheral equipment (e.g., a PC card), mobile equipment (e.g., a portable telephone), home appliance, equipment mounted on vehicles, artificial satellite and communication equipment.

BEST MODE FOR CARRYING OUT THE INVENTION

The present invention is described in detail below by referring to Examples and Comparative Examples, however, the present invention is not limited to these Examples.

In each Example, the tapping density, the angle of repose, the particle size and the pore diameter of the niobium powder and the capacitance, leakage current, capacitance appearance ratio, moisture resistance of the capacitor and ESR value of the capacitor were measured by the following methods.

(1) Measurement of Tapping Density

The tapping density was measured in accordance with the Method by Tapping Apparatus and the Measuring Instrument in the Apparent Specific Gravity Measuring Method of Industrial Sodium Carbonate specified in JIS (Japanese Industrial Standard, Edition of 2000) K1201-1.

(2) Measurement of Angle of Repose

The angle of repose was measured using the flowability measuring instrument and the sample amount specified in JIS (Japanese Industrial Standard, Edition of 2000) Z2504. More specifically, niobium powder was dropped on a horizontal plane from the hopper whose lower end was at a height of 6 cm above the horizontal plane and the angle of the slant face from the apex of the circular cone generated to the horizontal plane was designated as the angle of repose.

(3) Measurement of Particle Size

Using an apparatus manufactured by Microtrack (HRA 9320-X100), the particle size distribution was measured by the laser diffraction scattering method. A particle size value (D_{50} ; μm) when the accumulated volume % corresponded to 50 volume % was designated as the average particle size.

(4) Measurement of Pore Diameter

Using Poresizer 9320 manufactured by Micromeritics, the pore size distribution was measured by the mercury porosimetry method.

In the present invention, the maximal value was determined from the rate of change in the press-fitted

amount and by defining the pore diameter shown by the maximal value as the peak top, the maximal value was used as the size of relative intensity of the peak to which this peak top belongs.

5 (5) Measurement of Capacitance of Capacitor

The LCR meter manufactured by Hewlett-Packard was connected between terminals of the produced chip at room temperature and the measured capacitance at 120 Hz was defined as the capacitance of the capacitor processed into
10 a chip.

(6) Measurement of Leakage Current of Capacitor

The current value measured after a d.c. voltage of 6.3 V was continuously applied between terminals of the produced chip for 1 minute at room temperature was defined:
15 as the leakage current value of the capacitor processed into a chip.

(7) Capacitance Appearance Ratio of Capacitor

Assuming that the capacitance when a sintered body electrochemically formed in an aqueous 0.1% phosphoric acid
20 solution for 1,000 minutes under the conditions of 80°C and 20 V was measured in 30% sulfuric acid was 100%, the capacitance appearance ratio was expressed by the ratio to the capacitance after a capacitor was produced.

(8) Moisture Resistance Value of Capacitor

25 The moisture resistance value was expressed by the number of units where the capacitance after the produced capacitor was left standing at 60°C and 95% RH for 500 hours

was less than 110% or less than 120% of the initial value. As the number of units of less than 110% is larger, the moisture resistance value was judged better.

(9) Measurement of ESR Value of Capacitor

5 The LCR meter manufactured by Hewlett-Packard was connected between terminals of the produced chip at room temperature and the measured ESR value at 100 kHz, 1.5 VDC and 0.5 Vrms was defined as the ESR value of the capacitor.

10 Example 1:

 Into a nickel-made crucible, 5,000 g of potassium fluoroniobate thoroughly vacuum-dried at 80°C and sodium in a molar amount of 10 times the potassium fluoroniobate were charged and allowed to undertake a reduction reaction at 15 1,000°C for 20 hours under an argon atmosphere. After the completion of reaction, the reduction product was cooled, washed with water, washed with 95% sulfuric acid and then with water in sequence, vacuum-dried and pulverized for 40 hours using a ball mill of alumina pot containing silica 20 alumina balls. The pulverized product was dipped and stirred in a 3:2 (by mass) mixed solution of 50% nitric acid and 10% aqueous hydrogen peroxide. Thereafter, the pulverized product was thoroughly washed with water until the pH reached 7 to remove impurities, and then vacuum-dried. The starting material niobium powder had an average 25 particle size of 1.2 μm .

 In a niobium-made pot, 500 g of this starting material

niobium powder was placed and thereto, 50 g of butyl polymethylmethacrylate and 1 liter of toluene were added. Furthermore, zirconia balls were added and the contents were mixed for 1 hour using a shaking mixer. After removing 5 zirconia balls, the mixture was placed in a conical drier and vacuum-dried under the conditions of 1×10^2 Pa and 80°C.

Subsequently, this niobium powder was heated under 1×10^{-2} Pa at 250 to 400°C for 12 hours to decompose and remove butyl polymethylmethacrylate, and then sintered 10 under reduced pressure of 4×10^{-3} Pa at 1,150°C for 2 hours.

The niobium sintered lump was cooled until the product temperature was lowered to 30°C or lower, and then cracked using a roll granulator to obtain a niobium cracked powder having an average particle size of 100 μm .

15 This niobium cracked powder was subjected to a nitridation treatment at 300°C for 2 hours by passing nitrogen therethrough under pressure and about 450 g of niobium powder was obtained. The nitrogen content was 0.22%.

20 The physical properties of this niobium powder, such as tapping density, average particle size, angle of repose, BET specific surface area and pore diameter peak top are shown in Table 1.

The thus-obtained niobium powder (about 0.1 g) was charged into the hopper of a tantalum device automatic 25 molding machine (TAP-2R, manufactured by Seiken) and automatically molded together with a 0.3 mmΦ niobium wire to manufacture a molded article having a size of

approximately 0.3 cm × 0.18 cm × 0.45 cm. The outer appearance and the dispersion in the mass of the molded article are shown in Table 1.

This molded article was left standing in a vacuum of
5 4×10^{-3} Pa at 1,250°C for 30 minutes to obtain a sintered body. 100 Units of this sintered body were prepared and each was electrochemically formed using an aqueous 0.1% phosphoric acid solution at a voltage of 20 V for 200 minutes to form an oxide dielectric film on the surface.

10 Subsequently, an operation of dipping the sintered body in an aqueous 60% manganese nitrate solution and then heating it at 220°C for 30 minutes was repeated to form a manganese dioxide layer as the counter electrode layer on the oxide dielectric film. On this counter electrode layer,
15 a carbon layer and a silver paste layer were stacked in this order. After mounting a lead frame thereon, the device as a whole was molded with an epoxy resin to manufacture a chip-type capacitor. The capacitance appearance ratio of the capacitor, and the average capacitance and the average
20 leakage current (hereinafter simply referred to as "LC") of the chip-type capacitors (n=100 units) are shown in Table 1. The LC value is a value measured at room temperature by applying a voltage of 6.3 V for 1 minute.

Example 2:

25 In an SUS 304-made reactor, 1,000 g of a niobium ingot was placed and thereinto, hydrogen was continuously introduced at 400°C for 10 hours. After cooling, the

hydrogenated niobium lump was placed in an SUS 304-made pot containing zirconia balls and pulverized for 10 hours. Thereafter, this hydride was formed into a 20 vol% slurry with water, charged together with zirconia balls into a 5 spike mill and wet-pulverized at 40°C or lower for 7 hours to obtain a pulverized slurry of niobium hydride. This starting material niobium hydride powder had an average particle size of 0.9 µm.

In an SUS-made pot, this slurry (slurry concentration 10 of 98 %) was charged and thereto, 200 g of barium oxide having an average particle size of 1 µm was added. Furthermore, zirconia balls were added and the contents were mixed for 1 hour using a shaking mixer. After removing zirconia balls, the mixture was placed in a niobium-made 15 vat and vacuum-dried under the conditions of 1×10^2 Pa and 50°C.

Subsequently, the obtained mixture was heated under 1×10^{-2} Pa at 400°C for 4 hours to dehydrogenate the niobium hydride, and then sintered under reduced pressure of 4×10^{-3} 20 Pa at 1,100°C for 2 hours. The resulting barium oxide-mixed niobium sintered lump was cooled until the product temperature was lowered to 30°C or lower, and then cracked using a roll granulator to obtain a barium oxide-mixed niobium cracked powder having an average particle size of 25 95 µm.

Into a polytetrafluoroethylene container, 500 g of this barium oxide-mixed niobium cracked powder and 1,000 g

of ion-exchanged water were charged and cooled to 15°C or lower. Separately, an aqueous solution obtained by mixing 600 g of 60% nitric acid, 150 g of 30% hydrogen peroxide and 750 g of ion-exchanged water and cooled to 15°C or lower 5 was prepared. Then, 500 g of this aqueous solution was added dropwise with stirring to an aqueous solution having suspended therein the barium oxide-mixed niobium cracked powder while taking care not to allow the water temperature to exceed 20°C. After the completion of dropwise addition, 10 the solution was continuously stirred for another 1 hour, left standing for 30 minutes and then decanted. Thereto, 2,000 g of ion-exchanged water was added and the resulting solution was stirred for 30 minutes, left standing for 30 minutes and then decanted. This operation was repeated 5 times. Thereafter, the niobium cracked powder was charged 15 into a Teflon-made column and washed with water for 4 hours while flowing ion-exchanged water. At this time, the electrical conductivity of the washing water was 0.9 µS/cm.

After the completion of water washing, the niobium 20 cracked powder was dried at 50°C under reduced pressure and subjected to a nitridation treatment at 300°C for 3 hours by passing nitrogen therethrough under pressure, as a result, about 350 g of niobium powder was obtained. The nitrogen content was 0.28%.

25 The physical properties of this niobium powder, such as tapping-density, average particle size, angle of repose, BET specific surface area and average pore diameter, are

shown in Table 1.

The thus-obtained niobium powder (about 0.1 g) was charged into the hopper of a tantalum device automatic molding machine (TAP-2R, manufactured by Seiken) and 5 automatically molded together with a 0.3 mmΦ niobium wire to manufacture a molded article having a size of approximately 0.3 cm × 0.18 cm × 0.45 cm. The outer appearance and the dispersion in the mass of the molded article are shown in Table 1.

10 This molded article was left standing under reduced pressure of 4×10^{-3} Pa at 1,250°C for 30 minutes to obtain a sintered body. 100 Units of this sintered body were prepared and each was electrochemically formed using an aqueous 0.1% phosphoric acid solution at a voltage of 20 V, 15 for 200 minutes to form an oxide dielectric film on the surface.

Subsequently, an operation of contacting the oxide dielectric film with an equivalent mixed solution of an aqueous 10% ammonium persulfate solution and an aqueous 20 0.5% anthraquinonesulfonic acid solution and then with pyrrole vapor was repeated at least 5 times to form a counter electrode comprising polypyrrole on the oxide dielectric film.

On this counter electrode, a carbon layer and a silver 25 paste layer were stacked in this order. After mounting a lead frame thereon, the device as a whole was molded with an epoxy resin to manufacture a chip-type capacitor. The

capacitance appearance ratio of this capacitor, and the average capacitance and the average LC value of the chip-type capacitors (n=100 units) are shown in Table 1. The LC value is a value measured at room temperature by applying a 5 voltage of 6.3 V for 1 minute.

Examples 3 to 10:

Niobium powders, molded articles thereof, sintered bodies and capacitors were produced in the same manner as in Example 1 except for changing the average particle size 10 and the amount added of the butyl polymethylmethacrylate, or in the same manner as in Example 2 except for changing the average particle size and the amount added of the barium oxide. The physical properties of niobium powder and the outer appearance and the dispersion in the mass of 15 molded article, and the capacitance and the LC of capacitor are shown in Table 1.

Examples 11 to 22:

Niobium powders, molded articles and sintered bodies of Examples 11 to 14 and 16 to 18 were produced in the same 20 manner as in Example 1 and niobium powders, molded articles and sintered bodies of Examples 15 and 19 to 22 were produced in the same manner as in Examples 2, each except for using the activator shown in Table 1 in place of the butyl polymethylmethacrylate or barium oxide. The physical 25 properties of niobium powder, and the outer appearance and the dispersion in the mass of molded article are shown in Table 1.

These molded articles were then left standing under reduced pressure of 4×10^{-3} Pa at 1,250°C for 30 minutes to obtain sintered bodies. 100 Units of each sintered body were prepared and electrochemically formed using an aqueous 5 0.1% phosphoric acid solution at a voltage of 20 V for 200 minutes to form an oxide dielectric film on the surface.

Subsequently, each sintered body having formed thereon a dielectric material was dipped in an aqueous solution containing 25 mass% of ammonium persulfate (Solution 1), 10 pulled up, dried at 80°C for 30 minutes, dipped in an isopropanol solution containing 18 mass% of 3,4-ethylenedioxythiophene (Solution 2), pulled up and then left standing in an atmosphere of 60°C for 10 minutes, thereby performing the oxidation polymerization. This, 15 sintered body was again dipped in Solution 1 and then treated in the same manner as above. The operation from the dipping in Solution 1 until the oxidation polymerization was repeated 8 times. Then, the sintered body was washed with warm water at 50°C for 10 minutes and dried at 100°C 20 for 30 minutes, whereby a counter electrode comprising electrically conducting poly(3,4-ethylenedioxythiophene) was formed.

On this counter electrode, a carbon layer and a silver paste layer were stacked in this order. After mounting a 25 lead frame thereon, the device as a whole was molded with an epoxy resin to manufacture a chip-type capacitor. The capacitance appearance ratio of this capacitor, and the

average capacitance and the average LC value of the chip-type capacitors ($n=100$ units) are shown in Table 1. The LC value is a value measured at room temperature by applying a voltage of 6.3 V for 1 minute.

5 Examples 23 to 25:

Niobium powders, sintered bodies and capacitors were produced in the same manner as in Example 2 except for using, as the starting material, a niobium-tin alloy powder in Example 23, a niobium hydride-rhenium alloy powder in 10 Example 24, and a niobium hydride-yttrium-boron alloy powder in Example 25. The physical properties, the capacitance and the LC of the capacitors are shown in Table 1.

Comparative Examples 1 to 3:

15 Into a nickel-made crucible, 2,000 g of potassium fluoroniobate thoroughly vacuum-dried at 80°C and sodium in a molar amount of 10 times the potassium fluoroniobate were charged and allowed to undertake a reduction reaction at 1,000°C for 20 hours in an argon atmosphere. After the 20 completion of reaction, the reduction product was cooled, washed with water, washed with 95% sulfuric acid and then with water in sequence, vacuum-dried and pulverized using a ball mill of alumina pot containing silica alumina balls by varying the pulverization time period. The pulverized 25 products each was dipped and stirred in a 3:2 (by mass) mixed solution of 50% nitric acid and 10% aqueous hydrogen peroxide. Thereafter, each pulverized product was

thoroughly washed with water until the pH reached 7 to remove impurities, and then vacuum-dried. The produced niobium powder had an average particle size of 1.3 to 10 μm .

Subsequently, 50 g of the obtained niobium powder was placed in an SUS 304-made reactor and thereinto, nitrogen was continuously introduced at 300°C for 2 to 4 hours to obtain a niobium nitride.

The physical properties of each niobium powder, such as tapping density, average particle size, angle of repose, BET specific surface area and average pore diameter, are shown in Table 1.

The thus-obtained niobium powder (about 0.1 g) was charged into the hopper of a tantalum device automatic molding machine (TAP-2R, manufactured by Seiken) and the automatic molding together with a 0.3 mmΦ niobium wire was attempted. The results obtained are shown in Table 1.

Comparative Examples 4 to 9:

Niobium powders having a tapping density of 0.2 to 0.4 g/ml or 2.6 to 3.3 g/ml were obtained in the same manner as in Example 2 except for changing the amount added of the barium oxide having an average particle size of 1 μm . The physical properties thereof are shown in Table 1.

Each of the thus-obtained niobium powders (about 0.1 g) was charged into the hopper of a tantalum device automatic molding machine (TAP-2R, manufactured by Seiken) and automatically molded together with a 0.3 mmΦ niobium wire to manufacture molded articles having a size of

approximately 0.3 cm x 0.18 cm x 0.45 cm. The outer appearance and the dispersion in the mass of these molded articles are shown in Table 1.

These molded articles were left standing in a vacuum of 4×10^{-3} Pa at 1,250°C for 30 minutes to obtain sintered bodies. 100 Units of each sintered body were prepared and electrochemically formed using an aqueous 0.1% phosphoric acid solution at a voltage of 20 V for 200 minutes to form an oxide dielectric film on the surface.

Subsequently, an operation of contacting the oxide dielectric film with an equivalent mixed solution of an aqueous 10% ammonium persulfate solution and an aqueous 0.5% anthraquinonesulfonic acid solution and then with pyrrole vapor was repeated at least 5 times, whereby a counter electrode comprising polypyrrole was formed on the oxide dielectric film.

On this counter electrode, a carbon layer and a silver paste layer were stacked in this order. After mounting a lead frame thereon, the device as a whole was molded with an epoxy resin to manufacture a chip-type capacitor. The capacitance appearance ratio of the capacitor and the average capacitance and the average LC value of the chip-type capacitors (n=100 units) are shown in Table 1. The LC value is a value measured at room temperature by applying a voltage of 6.3 V for 1 minute.

Examples 26 to 31:

A hydride of niobium ingot was pulverized and

dehydrogenated to obtain primary particles having an average particle size of 0.8 μm . The obtained primary particles were sintered and pulverized to obtain a niobium granulated powder. Then, 0.1 g of this granulated powder 5 was charged in a metal mold (4.0 mm \times 3.5 mm \times 1.8 mm) together with a separately prepared niobium wire having a length of 10 mm and a thickness of 0.3 mm and a load was applied thereto as shown in Table 2 using a tantalum device automatic molding machine (TAP-2R, manufactured by Seiken) 10 to produce molded articles. The molded articles each was then sintered at 1,300°C for 30 minutes to obtain an objective sintered body. By controlling the load applied by the molding machine, sintered bodies having a pore diameter distribution shown in Table 2 were produced. The size, the 15 specific surface area and the CV value of the sintered body of Example 26 were 24.7 mm^3 , 1.1 m^2/g and 85,000 $\mu\text{FV/g}$, respectively. In other Examples, each value was within $\pm 2\%$ of Example 26.

Examples 32 to 34:

20 Sintered bodies were obtained in the same manner as in Examples 26 to 28 except for changing the average particle size of the primary particles to 0.5 μm by classifying the primary particles. The size, the specific surface area and the CV value of the sintered body of Example 32 were 25 24.9 mm^3 , 1.5 m^2/g and 125,000 $\mu\text{FV/g}$, respectively. In other Examples, each value was within $\pm 1\%$ of Example 32. The pore diameter distribution of each sintered body

produced is shown in Table 2.

Example 35:

A sintered body was obtained in the same manner as in Example 31 except for using a niobium powder obtained in 5 the same manner as in Example 4 in place of the granulated powder. The size, the specific surface area and the CV value of the sintered body of Example 35 were 24.8 mm³, 1.2 m²/g and 78,000 µFV/g, respectively. The pore diameter distribution of the sintered body produced is shown in 10 Table 2.

Comparative Examples 10 to 12:

Sintered bodies were produced in the same manner as in Examples 26 to 28 except that a niobium powder obtained by heat-treating at 1,100°C a niobium powder prepared by 15 reducing niobium chloride with magnesium was used in place of the niobium granulated powder used in Examples 26 to 28. The size, the specific surface area and the CV value of the sintered body of Comparative Example 10 were 24.3 mm³, 0.8 m²/g and 84,000 µFV/g, respectively. In other Examples, 20 each value was within ±2% of Comparative Example 10. The pore diameter distribution of each sintered body produced is shown in Table 2.

Example 36:

60 Units of respective sintered bodies produced in the 25 same manner as in Example 21 and Examples 26 to 35 each was electrochemically formed in an aqueous 0.1% phosphoric acid solution at 80°C and 20 V for 1,000 minutes to form an oxide

dielectric film on the surface of the sintered body. These sintered bodies after the electrochemical forming were divided into groups each consisting of 30 units. 30 Units of the sintered body in each group were impregnated with 5 two kinds of cathode agents A and B shown in Table 3. Thereon, carbon paste and silver paste were stacked in this order and the device was molded with an epoxy resin to manufacture a chip-type capacitor. The capacitance appearance ratio and the moisture resistance value of each 10 capacitor manufactured are shown in Table 4.

Comparative Example 13:

60 Units of respective sintered bodies produced in the same manner as in Comparative Examples 9 to 12 each was electrochemically formed in an aqueous 0.1% phosphoric acid, 15 solution at 80°C and 20 V for 1,000 minutes to form an oxide dielectric film on the surface of the sintered body. These sintered bodies after the electrochemical forming were divided into groups each consisting of 30 units. 30 Units of the sintered body in each group were impregnated with 20 cathode agent A shown in Table 3. Thereon, carbon pate and silver paste were stacked in this order and the device was molded with an epoxy resin to manufacture a chip-type capacitor. The capacitance appearance ratio and the moisture resistance value of each capacitor manufactured 25 are shown in Table 4.

Example 37:

Slurry was obtained by pulverizing the starting

material niobium hydride powder in the same manner as in Example 2. The niobium hydride powder had an average particle size of 0.6 μm . After centrifugal sedimentation of the slurry, the supernatant was removed by decantation.

5 Thereto, acetone anhydrous was added so to make a concentration of the slurry 40 % by mass and well suspended. After centrifugal sedimentation of the resulting solution, the supernatant was removed by decantation. This operation was repeated three times. Thereto, acetone anhydrous was
10 added so to make a concentration of the slurry 60 % by mass and well suspended. This slurry was charged in an SUS-made pot, and thereto, barium oxide having an average particle size of 1.4 μm and 23 μm were added in an amount of 15% by mass and 10% by mass of the niobium respectively.

15 Furthermore, zirconia balls were added and the contents were mixed for 1 hour using a shaking mixer. After removing zirconia balls, the mixture was placed in a niobium-made vat and vacuum-dried under the conditions of 1×10^2 Pa and 50°C.

20 The barium oxide-mixed niobium sintered lump and a niobium cracked powder were obtained in the same manner as in Example 2.

500 g of this barium oxide-mixed niobium cracked powder was added to 1,000 g of ion-exchanged water cooled
25 to 15°C or lower with stirring while taking care not to allow the water temperature to exceed 20°C. After the completion of addition, the slurry was continuously stirred

for another 1 hour, left standing for 30 minutes and then decanted. Thereto, 2,000 g of ion-exchanged water was added and the resulting slurry was stirred for 30 minutes, left standing for 30 minutes and then decanted. This operation 5 was repeated 5 times. Thereafter, the niobium cracked powder was charged into a Teflon-made column and washed with water for 4 hours while flowing ion-exchanged water. At this time, the electrical conductivity of the washing water was 0.5 μ S/cm.

10 After the completion of water washing, the niobium cracked powder was dried at 50°C under reduced pressure and subjected to a nitridation treatment at 300°C for 3 hours by passing nitrogen therethrough under pressure, as a result, about 350 g of niobium powder was obtained. The nitrogen 15 content was 0.30%.

The physical properties of this niobium powder, such as tapping density, average particle size, angle of repose, BET specific surface area and average pore diameter, are shown in Table 5.

20 A molded article was manufactured in the same manner as in Example 2. The outer appearance and the dispersion in the mass of the molded article are shown in Table 5.

Next a dielectric film was formed on the surface of a sintered body of the molded article in the same manner as 25 in Example 2. Then a counter electrode was formed and a carbon layer and a silver paste layer were stacked thereon in this order. After mounting a lead frame thereon, the

device as a whole was molded with an epoxy resin to manufacture a chip-type capacitor. The capacitance appearance ratio of this capacitor, and the average capacitance and the average LC value of the chip-type 5 capacitors (n=100 units) are shown in Table 5.

Examples 38 to 44:

A niobium cracked powder mixed with an activator was obtained in the same manner as in Example 37 by varying the 10 kind of the activator to be added, the average pore diameter and amount of the two kinds of niobium powder to be mixed. The solvent to dissolve the activator was selected from water, acid, alkali, solvent containing an ion exchange resin, solvent of ammonium nitrate and 15 solution containing ethylenediaminetetraacetate. The activator was dissolved in the same manner as in Example 37 to obtain a niobium powder. The physical properties of this niobium powder are shown in Table 5.

A molded article and a sintered body were manufactured 20 in the same manner as in Example 37 to fabricate a chip-type capacitor. The outer appearance and the dispersion in the mass of the molded article and the capacitance and the average LC value of the capacitor are shown in Table 5.

Examples 45 to 47:

25 A niobium alloy powder was obtained in the same manner as in Example 37—using as a starting material a niobium-neodymium alloy powder in Example 45, a niobium-tungsten

alloy powder in Example 46 and a niobium-tantalum alloy powder in Example 47 respectively. The physical properties of the niobium alloy powder are shown in Table 5.

A molded article and a sintered body were manufactured
5 in the same manner as in Example 37 to fabricate a chip-type capacitor. The outer appearance and the dispersion in the mass of the molded article and the capacitance and the average LC value of the capacitors are shown in Table 5.

10 Examples 48 to 58:

A niobium sintered body was produced in the same manner as in Example 2 using the niobium powder obtained in Example 37 to 47. The pore diameter distribution of the sintered body is shown in Table 6.

15

Examples 59 to 69:

100 units of each sintered body obtained in Examples 48 to 58 were prepared and electrochemically formed using an aqueous 0.1 mass % phosphoric acid solution at a voltage
20 of 20 V and 80 °C for 1,000 minutes to form an oxide dielectric film on the surface. These sintered bodies were impregnated with the cathode agents shown in Table 3. Thereon, a carbon layer and a silver paste layer were stacked in this order and the whole was molded with an
25 epoxy resin to manufacture a chip-type capacitor. The capacitance-appearance ratio and ESR of the manufactured capacitors are shown in Table 7.

Comparative Examples 14 to 17:

100 units of each sintered body obtained in Comparative Examples 9 to 12 were prepared and 5 electrochemically formed using an aqueous 0.1 mass % phosphoric acid solution at a voltage of 20 V and 80 °C for 1,000 minutes to form an oxide dielectric film on the surface. These sintered bodies were impregnated with the cathode agents shown in Table 3. Thereon, a carbon layer 10 and a silver paste layer were stacked in this order and the whole was molded with an epoxy resin to manufacture a chip-type capacitor. The capacitance appearance ratio and ESR of the manufactured capacitors are shown in Table 7.

Table 1

	Activator	Kind	Amount Added (mass%)	Average Particle Size (μm)	Tapping Density (g/ml)	Average Particle Size (μm)	Physical Properties of Niobium Powder		
							BET Area (m ² /g)	Specific Surface (m ² /g)	Pore Diameter Peak Top (μm)
Example 1	Butyl polymethylmethacrylate		10	1.0	0.7	120	42	1.4	1.2
Example 2	BaO	BaO	17	1.0	1.1	95	45	1.6	1.1
Example 3	Butyl polymethylmethacrylate		5	1.0	1.2	120	40	1.4	1.0
Example 4	Butyl polymethylmethacrylate		1	1.0	1.9	120	37	1.2	0.8
Example 5	BaO	BaO	35	1.0	0.5	95	53	1.8	0.9
Example 6	BaO	BaO	25	1.0	0.8	95	48	1.7	1.0
Example 7	BaO	BaO	17	3.0	1.1	95	45	1.6	2.8
Example 8	BaO	BaO	17	5.0	1.2	95	45	1.4	5.3
Example 9	BaO	BaO	17	9.0	1.5	95	40	1.2	7.5
Example 10	BaO	BaO	17	21	1.7	95	35	0.9	22
Example 11	camphor		40	100	1.9	180	32	1.3	78
Example 12	butyl polyacrylate		8	10	1.7	250	30	1.4	7.5
Example 13	polyvinyl alcohol		3	3.0	1.2	80	49	1.4	3.2
Example 14	ZnO	ZnO	15	3.0	1.1	85	44	1.7	2.4
Example 15	Re ₂ O ₇	Re ₂ O ₇	10	4.0	1.0	110	42	1.8	3.1
Example 16	WO ₂	WO ₂	7	3.0	1.3	100	45	1.6	3.1
Example 17	SnO ₂	SnO ₂	10	0.8	1.2	85	48	1.6	0.8
Example 18	MgO	MgO	20	3.0	1.1	90	45	1.8	2.6
Example 19	Mn(NO ₃) ₂	Mn(NO ₃) ₂	10	2.0	1.5	100	43	1.5	2.3
Example 20	CaCO ₃		10	1.0	1.0	85	42	1.7	0.8
Example 21	CaCO ₃		9	0.5	1.1	88	44	1.7	5.8
Example 22	B ₂ O ₃	Y ₂ O ₃	3	0.7	1.1	90	46	1.6	0.9
Example 23	BaO	BaO	17	1.0	1.0	95	46	1.4	1.4
Example 24	BaO		17	1.0	1.1	90	45	1.5	1.2
Example 25	Mn(NO ₃) ₂		17	0	-	2.6	1.3	1.3	0.9
Comp. Ex. 1	-	-	0	-	2.9	2.6	72	1.5	1.9
Comp. Ex. 2	-	-	0	-	3.0	1.0	69	0.49	9.0
Comp. Ex. 3	-	BaO	41	1.0	0.4	95	49	1.8	0.8
Comp. Ex. 4	BaO	BaO	45	1.0	0.3	90	56	1.9	0.8
Comp. Ex. 5	BaO	BaO	50	1.0	0.2	65	59	2.2	0.9
Comp. Ex. 6	BaO								

Comp. Ex. 7	BaO	0.8	1.0	2.6	85	48	1.2	0.7
Comp. Ex. 8	BaO	0.6	1.0	3.0	90	48	1.0	0.6
Comp. Ex. 9	BaO	0.4	1.0	3.3	100	44	0.9	0.6

Table 1 (continued)

	Sintered Body		Electrical Properties		
	Outer Appearance: chipping, cracking, distortion	Dispersion in Mass (g/sintered body)	Capacitance Appearance Ratio (%)	Capacitance (μF)	LC (μA)
Example 1	none	0.1±0.002	92	409	13
Example 2	none	0.1±0.002	91	460	19
Example 3	none	0.1±0.002	92	409	17
Example 4	none	0.1±0.002	89	387	15
Example 5	none	0.1±0.002	90	472	21
Example 6	none	0.1±0.002	92	460	22
Example 7	none	0.1±0.002	88	563	26
Example 8	none	0.1±0.002	91	523	18
Example 9	none	0.1±0.002	93	419	13
Example 10	none	0.1±0.002	91	263	5
Example 11	none	0.1±0.002	90	392	19
Example 12	none	0.1±0.002	90	387	12
Example 13	none	0.1±0.002	93	539	25
Example 14	none	0.1±0.002	89	516	22
Example 15	none	0.1±0.002	92	501	14
Example 16	none	0.1±0.002	89	512	17
Example 17	none	0.1±0.002	92	408	11
Example 18	none	0.1±0.002	95	608	23
Example 19	none	0.1±0.002	91	382	17
Example 20	none	0.1±0.002	94	588	29
Example 21	none	0.1±0.002	97	590	23
Example 22	none	0.1±0.002	90	446	21
Example 23	none	0.1±0.002	91	450	13
Example 24	none	0.1±0.002	93	558	15
Example 25	none	0.1±0.002	91	446	13
Comp. Ex.	could not be molded		-	-	-
Comp. Ex. 1	could not be molded		-	-	-
Comp. Ex. 2	could not be molded		-	-	-
Comp. Ex. 3	could not be molded		-	-	-

Comp. 4	Ex.	present	0.1 ± 0.015	91	396	18
Comp. 5	Ex.	present	0.1 ± 0.026	92	409	18
Comp. 6	Ex.	present	0.1 ± 0.046	95	432	17
Comp. 7	Ex.	none	0.1 ± 0.002	42	143	9
Comp. 8	Ex.	none	0.1 ± 0.002	37	115	7
Comp. 9	Ex.	none	0.1 ± 0.002	22	64	5

Table 2

Examples and Comparative Examples	Molding Load Applied, N	Pore Distribution		
		Pore Diameter of Peak 1, μm	Pore Diameter of Peak 2, μm	Peak having Larger Relative Intensity
Example 26	392	0.63	1.0	Peak 2
Example 27	686	0.42	1.3	Peak 2
Example 28	981	0.28	0.77	Peak 2
Example 29	490	0.35	2.3	Peak 2
Example 30	785	0.49	0.96	Peak 2
Example 31	294	0.52	2.8	Peak 2
Example 32	392	0.60	2.1	Peak 2
Example 33	686	0.44	2.8	Peak 2
Example 34	981	0.34	1.1	Peak 1
Example 35	294	0.61	2.7	Peak 2
Comparative Example 10	392	0.65	none	-
Comparative Example 11	686	0.42	none	-
Comparative Example 12	981	0.25	none	-

Table 3

Method	Cathode Agent	Method for Impregnating Cathode Agent
A	Polypyrrole	Vapor phase polymerization with pyrrole vapor on the sintered body having attached thereto ammonium persulfate and anthraquinonesulfonic acid, was repeated.
B	mixture of lead dioxide and lead sulfate (lead dioxide: 98 mass%)	Dipping of sintered body in a mixed solution of lead acetate and ammonium persulfate was repeated.

Table 4

Manufacturing Method of Sintered Body	Method of Impregnating Cathode Agent	Capacitance Appearance Ratio, %	Moisture Resistance Value	
			Number of units having capacitance of 100% to less than 110%	Number of units having capacitance of 110% to less than 120%
Example 21	A	97	30/30	0/30
Example 26	A	82	30/30	0/30
	B	88	30/30	0/30
Example 27	A	84	30/30	0/30
	B	87	30/30	0/30
Example 28	A	79	27/30	3/30
Example 29	A	83	30/30	0/30
Example 30	A	80	30/30	0/30
Example 31	A	81	30/30	0/30
Example 32	A	85	30/30	0/30
Example 33	A	81	30/30	0/30
Example 34	A	82	28/30	2/30
Example 35	A	95	30/30	0/30
Comparative Example 9	A	22	4/30	26/30
Comparative Example 10	A	71	15/30	15/30
Comparative Example 11	A	73	17/30	13/30
Comparative Example 12	A	68	19/30	11/30

Table 5

	Activator		Physical Properties of Niobium Powder					
	Kind	Amount Added (mass%)	Average Particle Size (μm)	Tapping Density (g/mL)	Average Particle Size (μm)	Angle of Repose ($^\circ$)	BET Specific Surface Area (m^2/g)	Pore Diameter Peak Top (μm)
Example 37	BaO	15 10	1.4 2.3	0.9	98	49	1.7	1.5 25
Example 38	BaO	17 15	2.0 3.0	1.0	130	47	1.6	2.2 34
Example 39	CaCO ₃	20 10	3.0 15	1.2	202	44	1.5	3.1 18
Example 40	MgO B ₂ O ₃	18 8	1.5 10	1.0	121	45	1.7	1.6 12
Example 41	Al ₂ O ₃	20 20	2.0 25	0.9	140	49	1.7	2.1 24
Example 42	MgO Al ₂ O ₃	15 15	1.5 2.0	0.9	138	47	1.8	1.8 22
Example 43	Y ₂ O ₃ Al ₂ O ₃	15 10	2.0 25	1.1	98	47	1.6	1.9 24
Example 44	MgO	15 20	1.5 2.5	0.9	135	46	1.9	1.9 22
Example 45	BaO	15 10	1.4 2.3	0.9	150	45	1.9	1.3 22
Example 46	BaO	15 10	1.4 2.3	0.9	111	49	1.7	1.7 26
Example 47	BaO	15 10	1.4 2.3	0.9	130	46	1.7	1.4 21

Table 5 (continued)

	Sintered Body	Dispersion in Mass (g/sintered body)	Capacitance Ratio (%)	Capacitance (μ F)	Electrical Properties
	Outer Appearance: chipping, cracking, distortion				LC (μ A)
Example 37	none	0.1±0.002	98	592	23
Example 38	none	0.1±0.002	97	587	23
Example 39	none	0.1±0.002	93	557	22
Example 40	none	0.1±0.002	93	556	20
Example 41	none	0.1±0.002	98	585	24
Example 42	none	0.1±0.002	98	589	20
Example 43	none	0.1±0.002	97	581	22
Example 44	none	0.1±0.002	98	590	20
Example 45	none	0.1±0.002	98	592	18
Example 46	none	0.1±0.002	98	587	19
Example 47	none	0.1±0.002	98	587	24

Table 6

Examples	Method to obtain a niobium powder	Pore Distribution		
		Pore Diameter of Peak 1, μm	Pore Diameter of Peak 2, μm	Peak having Larger Relative Intensity
Example 48	Example 37	0.73	3.1	Peak 2
Example 49	Example 38	0.89	5.1	Peak 2
Example 50	Example 39	1.05	2.4	Peak 2
Example 51	Example 40	0.71	2.1	Peak 2
Example 52	Example 41	0.91	2.9	Peak 2
Example 53	Example 42	0.69	2.7	Peak 2
Example 54	Example 43	0.88	2.9	Peak 2
Example 55	Example 44	0.72	3.2	Peak 2
Example 56	Example 45	0.71	3.0	Peak 2
Example 57	Example 46	0.72	3.3	Peak 2
Example 58	Example 47	0.71	3.1	Peak 2

Table 7

Examples and Comparative Examples	Method to obtain a sintered body	Capacitance appearance Ratio, %	Capacitance	ESR Ω
Example 59	Example 48	98	592	0.024
Example 60	Example 49	97	587	0.023
Example 61	Example 50	93	557	0.022
Example 62	Example 51	93	556	0.022
Example 63	Example 52	98	585	0.023
Example 64	Example 53	98	589	0.023
Example 65	Example 54	97	581	0.024
Example 66	Example 55	98	590	0.022
Example 67	Example 56	98	592	0.024
Example 68	Example 57	98	587	0.023
Example 69	Example 58	98	587	0.025
Comparative Example 14	Comparative Example 9	22	64	0.158
Comparative Example 15	Comparative Example 10	71	305	0.083
Comparative Example 16	Comparative Example 11	73	314	0.081
Comparative Example 17	Comparative Example 12	68	291	0.090

INDUSTRIAL APPLICABILITY

A niobium powder of the present invention having a tapping density of 0.5 to 2.5 g/ml, an average particle size of 10 to 1000 μm , angle of repose from 10 to 60° and the BET specific surface area from 0.5 to 40 m^2/g is excellent in flowability and capable of continuous molding.

By using a niobium sintered body, which is obtained by sintering the niobium powder and has a pore diameter peak top in a range of 0.01 μm to 500 μm , preferably having a plurality of pore diameter peak tops in the pore

distribution, for the capacitor electrode, a high capacitance appearance ratio can be obtained and a capacitor having low leakage current and excellent moisture resistance can be produced.

5

CLAIMS

1. A niobium powder for a capacitor having a tapping density of 0.5 to 2.5 g/ml.

5

2. The niobium powder as claimed in claim 1, wherein the average particle size is from 10 to 1,000 μm .

3. The niobium powder as claimed in claim 1 or 2, wherein
10 the angle of repose is from 10° to 60°.

4. The niobium powder as claimed in any one of claims 1 to 3, wherein the BET specific surface area is from 0.5 to 40 m^2/g .

15

5. The niobium powder as claimed in any one of claims 1 to 4, which has a pore distribution having a pore diameter peak top in the range of 0.01 μm to 500 μm .

20 6. The niobium powder as claimed in claim 5, wherein the pore distribution has a plurality of pore diameter peak tops.

7. The niobium powder as claimed in claim 5 or 6, wherein
25 any of the pore diameter peak tops is in the range of 0.5 to 100 μm .

8. The niobium powder as claimed in any one of claims 1

to 7, wherein at least one element selected from the group consisting of nitrogen, carbon, boron and sulfur elements is contained in an amount of 200,000 mass ppm or less.

5 9. A sintered body using the niobium powder as claimed in any one of claims 1 to 8.

10. The sintered body as claimed in claim 9, which has a pore distribution having a pore diameter peak top in the 10 range of 0.01 μm to 500 μm .

11. A niobium sintered body for a capacitor electrode, wherein the pore distribution of the niobium sintered body has a plurality of pore diameter peak tops.

15

12. The niobium sintered body as claimed in claim 11, wherein the pore distribution has two pore diameter peak tops.

20 13. The niobium sintered body as claimed in claim 11 or 12, wherein among the plurality of pore diameter peak tops, the peak tops of the two peaks having a highest relative intensity are present in the range of 0.2 to 0.7 μm and in the range of 0.7 to 3 μm respectively.

25

14. The niobium sintered body as claimed in any one of claims 11 to 13, wherein among the plurality of pore diameter peak tops, the peak top of the peak having a

highest relative intensity is present in the larger diameter side than the peak top of the peak having a next highest relative intensity.

5 15. The niobium sintered body as claimed in any one of claims 9 to 14, wherein the sintered body has a volume of 10 mm³ or more including the volume of pore void.

10 16. The niobium sintered body as claimed in any one of claims 9 to 15, wherein the sintered body has a specific surface area of 0.2 to 7 m²/g.

15 17. The niobium sintered body as claimed in any one of claims 9 to 16, wherein a part of the sintered body is nitrided.

20 18. The niobium sintered body as claimed in any one of claims 12 to 17, wherein the sintered body is a sintered body obtained from a niobium molded article which gives a sintered body having a CV value of 40,000 to 200,000 µFV/g when sintered at 1,300°C.

25 19. A capacitor comprising one electrode using the niobium sintered body claimed in any one of claims 9 to 18, a counter electrode and a dielectric material interposed therebetween.

20. The capacitor as claimed in claim 19, wherein the

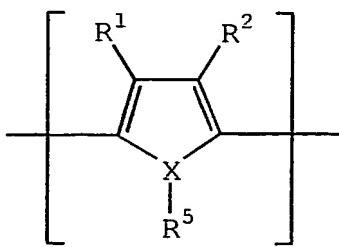
dielectric material mainly comprises niobium oxide.

21. The capacitor as claimed in claim 19, wherein the counter electrode is at least one material selected from 5 the group consisting of an electrolytic solution, an organic semiconductor and an inorganic semiconductor.

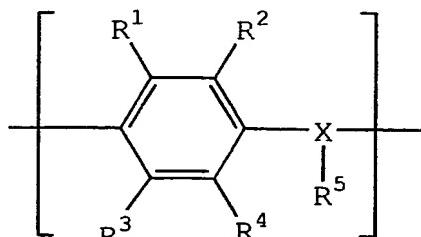
22. The capacitor as claimed in claim 21, wherein the counter electrode is an organic semiconductor and the 10 organic semiconductor is at least one material selected from the group consisting of an organic semiconductor comprising a benzopyrrolidine tetramer and chloranile, an organic semiconductor mainly comprising tetrathiotetracene, an organic semiconductor mainly comprising tetracyanoquino- 15 dimethane, and an electrically conducting polymer.

23. The capacitor as claimed in claim 22, wherein the electrically conducting polymer is at least one member selected from the group consisting of polypyrrole, 20 polythiophene, polyaniline and substitution derivatives thereof.

24. The capacitor as claimed in claim 22, wherein the electrically conducting polymer is an electrically 25 conducting polymer obtained by doping a dopant into a polymer containing a repeating unit represented by the following formula (1) or (2):



(1)

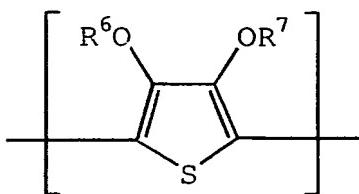


(2)

(wherein R¹ to R⁴ each independently represents a monovalent group selected from the group consisting of a hydrogen atom, a linear or branched, saturated or unsaturated alkyl, alkoxy or alkylester group having from 1 to 10 carbon atoms, a halogen atom, a nitro group, a cyano group, a primary, secondary or tertiary amino group, a CF₃ group, a phenyl group and a substituted phenyl group; each of the pairs of R¹ and R², and R³ and R⁴ may combine at an arbitrary position to form a divalent chain for forming at least one 3-, 4-, 5-, 6- or 7-membered saturated or unsaturated hydrocarbon cyclic structure together with the carbon atoms substituted by R¹ and R² or by R³ and R⁴; the cyclic combined chain may contain a bond of carbonyl, ether, ester, amide, sulfide, sulfinyl, sulfonyl or imino at an arbitrary position; X represents an oxygen atom, a sulfur atom or a nitrogen atom; R⁵ is present only when X is a nitrogen atom, and independently represents a hydrogen atom or a linear or branched, saturated or unsaturated alkyl group having from 1 to 10 carbon atoms).

25. —The capacitor as claimed in claim 24, wherein the electrically conducting polymer is an electrically

conducting polymer containing a repeating unit represented by the following formula (3):



(3)

(wherein R⁶ and R⁷ each independently represents a hydrogen atom, a linear or branched, saturated or unsaturated alkyl group having from 1 to 6 carbon atoms, or a substituent for forming at least one 5-, 6- or 7-membered saturated hydrocarbon cyclic structure containing two oxygen elements resulting from the alkyl groups combining with each other at an arbitrary position; and the cyclic structure includes a structure having a vinylene bond which may be substituted, and a phenylene structure which may be substituted).

26. The capacitor as claimed in claim 22, wherein the electrically conducting polymer is an electrically conducting polymer obtained by doping a dopant into poly(3,4-ethylenedioxythiophene).

27. The capacitor as claimed in claim 19, wherein the counter electrode is formed of a material at least partially having a layer structure.

28. The capacitor as claimed in claim 19, wherein the material of the counter electrode contains an organic

sulfonate anion as a dopant.

29. A method for producing the niobium powder claimed in any one of claims 1 to 8, comprising activation-treatment 5 of niobium or a niobium compound.

30. The method for producing the niobium powder as claimed in claim 29, wherein the activation treatment of niobium or a niobium compound is performed by at least one step 10 selected from the group consisting of a sintering step and a cracking step.

31. The method for producing the niobium powder as claimed in claim 29 or 30, wherein the activation treatment of 15 niobium or a niobium compound is performed using a mixture of niobium or a niobium compound and an activator.

32. The method for producing the niobium powder as claimed in any one of claims 29 to 31, wherein the average particle 20 size of the niobium or niobium compound processed with the activation treatment is from 0.01 µm to 10 µm.

33. The method for producing the niobium powder as claimed in any one of claims 29 to 32, wherein the niobium or 25 niobium compound contains at least one element selected from the group consisting of nitrogen, carbon, boron and sulfur in an amount of 200,000 ppm or less.

34. The method for producing the niobium powder as claimed in any one of claims 29 to 33, wherein the niobium compound is at least one member selected from the group consisting of niobium hydride, niobium alloy and niobium hydride alloy.

5

35. The method for producing the niobium powder as claimed in claim 34, wherein the component other than niobium contained in the niobium alloy or niobium hydride alloy is at least one element selected from the group consisting of 10 elements having an atomic number of 88 or less excluding hydrogen, nitrogen, oxygen, fluorine, chlorine, bromine, iodine, niobium, helium, neon, argon, krypton, xenon and radon.

15 36. The method for producing the niobium powder as claimed in claim 31, wherein the mixture containing niobium or a niobium compound and an activator is obtained by mixing these using a solvent.

20 37. The method for producing the niobium powder as claimed in claim 36, wherein the solvent is at least one solvent selected from the group consisting of water, alcohols, ethers, cellosolves, ketones, aliphatic hydrocarbons, aromatic hydrocarbons and halogenated hydrocarbons.

25 38. The method for producing the niobium powder as claimed in claim 31, wherein the activator is used in an amount of 1 to 40 mass% based on the total amount of the niobium or niobium compound.

39. The method for producing the niobium powder as claimed in claim 31 or 38, wherein the average particle size of the activator is from 0.01 μm to 500 μm .

5

40. The method for producing the niobium powder as claimed in any one of claims 31, 38 and 39, wherein the activator has a plurality of particle size peak tops.

10 41. The method for producing the niobium powder as claimed in any one of claims 31 or 38 to 40, wherein the activator is a substance which is removed as a gas at 2,000°C or less.

15 42. The method for producing the niobium powder as claimed in claim 41, wherein the activator is at least one member selected from the group consisting of naphthalene, anthracene, quinone, camphor, polyacrylic acid, polyacrylic acid ester, polyacrylamide, polymethacrylic acid, polymethacrylic acid ester, polymethacrylamide, polyvinyl 20 alcohol, NH₄Cl, ZnO, WO₂, SnO₂ and MnO₃.

25 43. The method for producing the niobium powder as claimed in any one of claims 31 or 38 to 40, wherein the activator is at least one member selected from the group consisting of a water-soluble substance, an organic solvent-soluble substance, an acidic solution-soluble substance, an alkaline solution-soluble substance, a substance which forms a complex and becomes a substance soluble in water,

organic solvent, acidic solution or alkaline solution, and a substance which becomes a substance soluble in water, organic solvent, acidic solution or alkaline solution at 2,000°C or less.

5

44. The method for producing the niobium powder as claimed in claim 43, wherein the activator is at least one member selected from the group consisting of compounds of a metal with carbonic acid, sulfuric acid, sulfurous acid, halogen, 10 perhalogen acid, hypohalogen acid, nitric acid, nitrous acid, phosphoric acid, acetic acid, oxalic acid or boric acid, metals, metal hydroxides and metal oxides.

45. The method for producing the niobium powder as claimed 15 in claim 43, wherein the activator is at least one member selected from the group consisting of lithium, sodium, potassium, rubidium, cesium, francium, beryllium, magnesium, calcium, strontium, barium, radium, scandium, yttrium, cerium, neodymium, titanium, zirconium, hafnium, vanadium, 20 niobium, tantalum, molybdenum, tungsten, manganese, rhenium, ruthenium, osmium, cobalt, rhodium, iridium, nickel, palladium, platinum, silver, gold, zinc, cadmium, boron, aluminum, gallium, indium, thallium, silicon, germanium, tin, lead, arsenic, antimony, bismuth, selenium, tellurium, 25 polonium and compounds thereof.

46. The method for producing the niobium powder as claimed in claim 29, wherein the activation treatment is a

treatment of removing the activator by heating and/or under reduced pressure before or during the sintering step.

47. The method for producing the niobium powder as claimed
5 in claim 29, wherein the activation treatment is a treatment of removing the activator component by contacting a solvent with the sintered or cracked product after the sintering step and during or after the cracking step.

10 48. The method for producing the niobium powder as claimed in claim 47, wherein the solvent is at least one member selected from the group consisting of water, an organic solvent, an acidic solution, an alkaline solution and a solution containing a ligand of forming a soluble complex.

15

49. The method for producing the niobium powder as claimed in claim 48, wherein the acidic solution is a solution of at least one member selected from the group consisting of nitric acid, sulfuric acid, hydrofluoric acid and hydrochloric acid.

20 50. The method for producing the niobium powder as claimed in claim 48, wherein the alkaline solution contains at least one member selected from the group consisting of an alkali metal hydroxide and ammonia.

25

51. The method for producing the niobium powder as claimed in claim 48, wherein the ligand is at least one member selected from the group consisting of ammonia, glycine and

ethylenediaminetetraacetic acid.

52. The method for producing the niobium powder as claimed
in claim 48, wherein the organic solvent is methyl isobutyl
5 ketone.

53. A method for producing a nitrogen-containing niobium
powder, comprising treating the niobium powder claimed in
any one of claims 1 to 7 by at least one method selected
10 from the group consisting of liquid nitridation, ion
nitridation and gas nitridation.

54. A method for producing a carbon-containing niobium
powder, comprising treating the niobium powder claimed in
15 any one of claims 1 to 7 by at least one method selected
from the group consisting of solid phase carbonization and
liquid carbonization.

55. A method for producing a boron-containing niobium
20 powder, comprising treating the niobium powder claimed in
any one of claims 1 to 7 by at least one method selected
from the group consisting of gas boronization and solid
phase boronization.

25 56. A method for producing a sulfur-containing niobium
powder, comprising treating the niobium powder claimed in
any one of claims 1 or 7 by at least one method selected
from the group consisting of gas sulfidization, ion

sulfudization and solid phase sulfudization.

57. A niobium powder obtained by the production method as claimed in any one of claims 29 to 56.

5

58. A method for producing a niobium sintered body, using the niobium powder claimed in any one of claims 1 to 8 and 57.

10 59. A method for producing a capacitor comprising one electrode using a niobium sintered body, a dielectric material formed on the surface of the sintered body and a counter electrode provided on the dielectric material, wherein the niobium sintered body is obtained by sintering
15 the niobium powder claimed in any one of claims 1 to 8 and 57.

20 60. The method for producing a capacitor as claimed in claim 59, wherein the dielectric material is formed by electrolytic oxidation.

25 61. A method for producing a capacitor comprising one electrode using a niobium sintered body, a dielectric material formed on the surface of the sintered body and a counter electrode provided on the dielectric material, wherein the niobium sintered body is the niobium sintered body claimed in any one of claims 9 to 18.

62. An electronic circuit using the capacitor as claimed
in any one of claims 19 to 28.

63. An electronic instrument using the capacitor as
5 claimed in any one of claims 19 to 28.

Fig.1

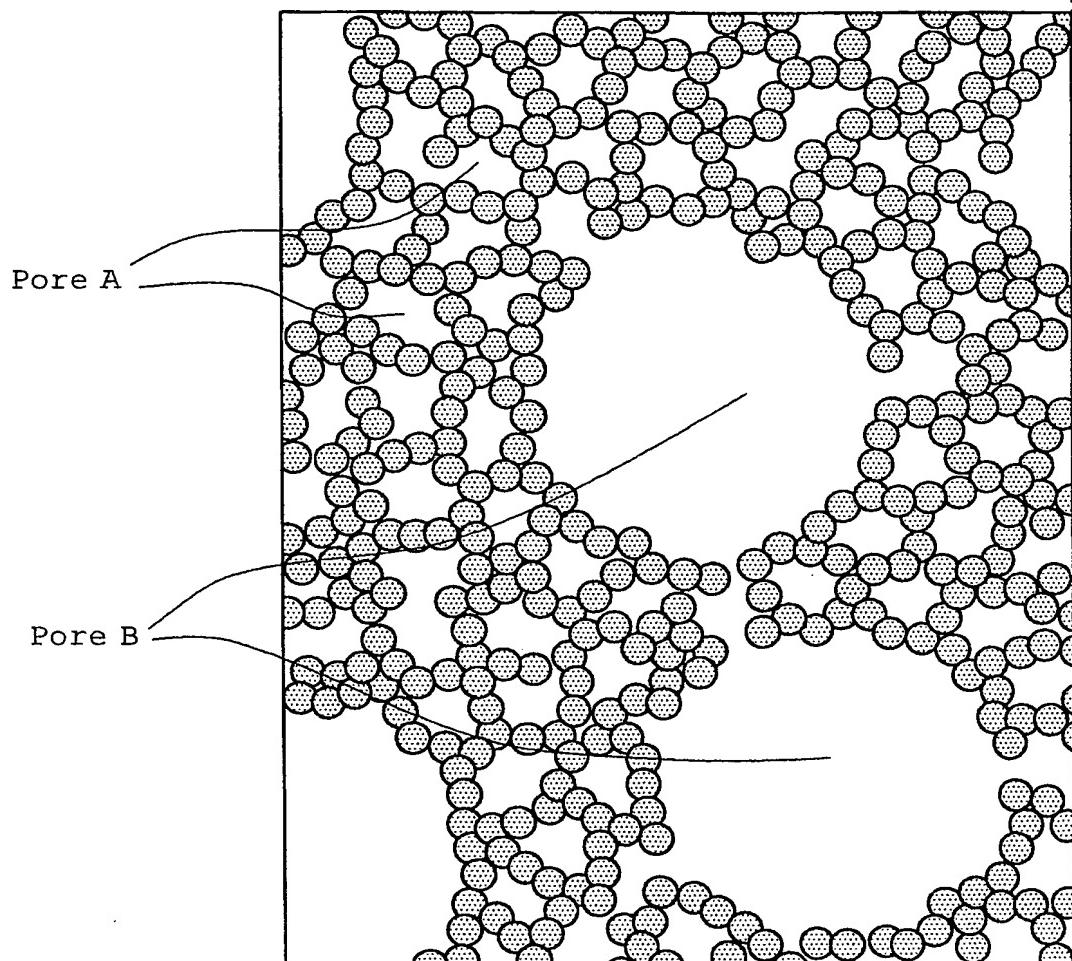
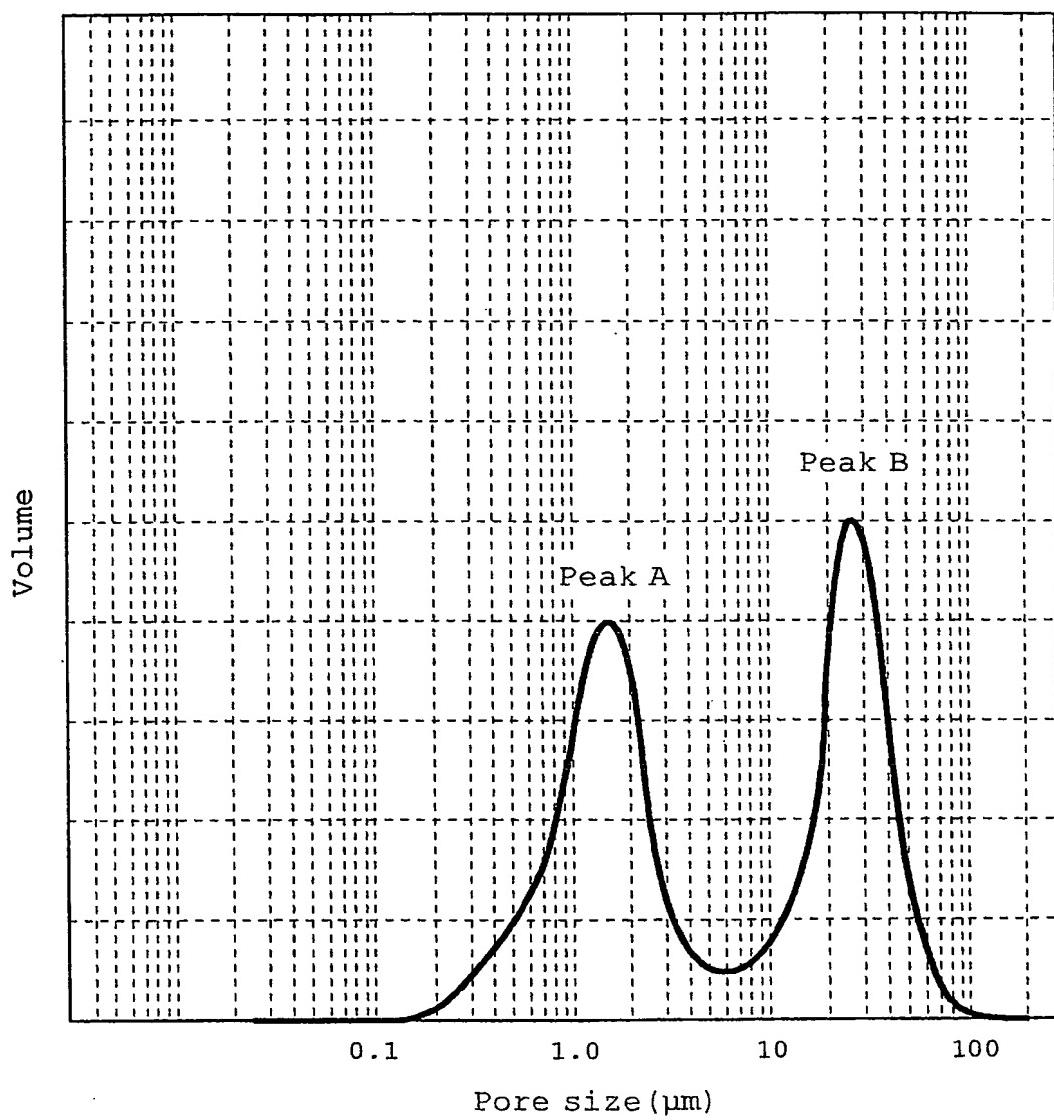


Fig.2



(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
21 November 2002 (21.11.2002)

PCT

(10) International Publication Number
WO 02/092864 A3

(51) International Patent Classification⁷: **C22C 1/04**, B22F 1/00, H01G 9/052

(21) International Application Number: **PCT/JP02/04644**

(22) International Filing Date: 14 May 2002 (14.05.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2001-145571 15 May 2001 (15.05.2001) JP
60/291,925 21 May 2001 (21.05.2001) US
2001-340318 6 November 2001 (06.11.2001) JP
60/331,200 9 November 2001 (09.11.2001) US

(71) Applicant (for all designated States except US): **SHOWA DENKO K. K.** [JP/JP]; 13-9, Shiba Daimon 1-chome, Minato-ku, Tokyo 105-8518 (JP).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **OMORI, Kazuhiro** [JP/JP]; Corporate R & D Center, Showa Denko K.K., 5-1, Okawa-cho, Kawasaki-ku, Kawasaki-shi, Kanagawa 210-0858 (JP). **NAITO, Kazumi** [JP/JP]; Central Research Laboratory, Showa Denko K. K., 1-1, Ohnodai 1-chome, Midori-ku, Chiba-shi, Chiba 267-0056 (JP). **KAWASAKI, Toshiya** [JP/JP]; Corporate R & D Center, Showa Denko K.K., 5-1, Okawa-cho, Kawasaki-ku, Kawasaki-shi, Kanagawa 210-0858 (JP). **WADA, Kouichi** [JP/JP]; Corporate R & D Center, Showa Denko K.K., 5-1, Okawa-cho, Kawasaki-ku, Kawasaki-shi, Kanagawa 210-0858 (JP).

(74) Agent: **OHIE, Kunihisa**; Ohie Patent Office, Horiguchi No. 2, Building 7fl, 2-6, Nihonbashi-Ningyocho 2-chome, Chuo-ku 103-0013 (JP).

(81) Designated States (national): AB, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HU, ID, IL, IN, IS, KE, KG, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PL, SE, TR), OAPI patent (BJ, BJ, CN, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

(88) Date of publication of the international search report:
25 September 2003

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

A3

WO 02/092864

(54) Title: NIOBIUM POWDER, NIOBIUM SINTERED BODY AND CAPACITOR USING THE SINTERED BODY

(57) Abstract: A niobium powder for a capacitor having a tapping density of 0.5 to 2.5 g/ml, and average particle size of 10 to 1000 μm , angle of repose from 10° to 60°, the BET specific surface area from 0.5 to 40 m^2/g and a plurality of pore diameter peak tops in the pore distribution, and a producing method thereof; (2) a niobium sintered body, which is obtained by sintering the above niobium powder and, having a plurality of pore diameter peak tops in a range of 0.01 μm to 500 μm , preferably, the peak tops of two peaks among the plurality of pore diameter peak tops having a highest relative intensity are present in the range of 0.2 to 0.7 μm and in the range of 0.7 to 3 μm , respectively, and a producing method thereof; (3) a capacitor using the above sintered body and a producing method thereof; and (4) an electronic circuit and electronic device using the above capacitor.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/JP 02/04644

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C22C1/04 B22F1/00 H01G9/052

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01G C22C B22F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 165 623 A (FIFE JAMES A, ET AL) 26 December 2000 (2000-12-26) column 6, line 67 column 8, line 3 – line 4 claims 4,10,19,22,43,50,51	1,2,4,9, 16, 18-20, 58-63
Y	---	21-24 -/-

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

8 July 2003

Date of mailing of the international search report

15/07/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Goossens, A

INTERNATIONAL SEARCH REPORT

International Application No

PCT/JP 02/04644

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00 67936 A (STARCK H C GMBH CO KG ; THOMAS OLIVER (DE); REICHERT KARLHEINZ (DE)) 16 November 2000 (2000-11-16) page 16, line 22 - line 23 page 17, line 4 - line 15 page 17, line 22 - line 24 page 19, line 16 - line 20 page 19, line 27 claims 54,55	1,2,4,8, 9,15-20, 27,29, 53,57-63
Y	page Y, line 21-24	31-35, 38,43, 45-48
Y	WO 01 12364 A (STARCK H C INC) 22 February 2001 (2001-02-22) page 2, line 17 - line 20 embodiment J page 2, line 35 -page 3, line 6 page 4, line 30 - line 31 embodiment J	31-35, 38,43, 45-48
P,Y	EP 1 204 126 A (SHOWA DENKO KK) 8 May 2002 (2002-05-08) paragraph '0034! - paragraph '0036!	21-24
Y	& WO 01 06525 A (SHOWA DENKO KABUSHIKI KAISHA) 25 January 2001 (2001-01-25)	21-24

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/JP 02/04644

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
US 6165623	A	26-12-2000	AU BR EE EP EP JP WO US TW	5162798 A 9712906 A 9900189 A 1075884 A2 0946323 A1 2002507247 T 9819811 A1 6420043 B1 463194 B		29-05-1998 02-01-2002 15-12-1999 14-02-2001 06-10-1999 05-03-2002 14-05-1998 16-07-2002 11-11-2001
WO 0067936	A	16-11-2000	WO AU AU BR CA EP JP US	0067936 A1 757790 B2 5896599 A 9911008 A 2331707 A1 1144147 A1 2002544375 T 6558447 B1		16-11-2000 06-03-2003 21-11-2000 30-04-2002 16-11-2000 17-10-2001 24-12-2002 06-05-2003
WO 0112364	A	22-02-2001	US AU BR CA CN CZ EA EP WO US US	6261337 B1 7063600 A 0007018 A 2346957 A1 1322157 T 20011740 A3 2736 B1 1200218 A1 0112364 A1 2003056619 A1 2002041819 A1		17-07-2001 13-03-2001 03-07-2001 22-02-2001 14-11-2001 13-02-2002 29-08-2002 02-05-2002 22-02-2001 27-03-2003 11-04-2002
EP 1204126	A	08-05-2002	AU EP US CN WO TW	6017200 A 1204126 A1 2002104404 A1 1363102 T 0106525 A1 464889 B		05-02-2001 08-05-2002 08-08-2002 07-08-2002 25-01-2001 21-11-2001